DIRECT PRODUCTION OF AROMATIC HYDROCARBONS/GASOLINE FROM SYNTHESIS GAS

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Report Submitted by

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SECTION I

This section covers the work done under the following Tasks:

Task A: Review of the current literature on the subject.

Task B: Preparation and characterization of HZSM-5 catalyst.

Task C: Preparation and screening of Fischer-Tropsch (FT) catalysts using a microreactor.

Task D: Testing of FT-HZSM-5 catalyst combination in a microreactor.

Task E: Design and construction of a 1/2 inch packed bed reactor.

INTRODUCTION

The indirect process for conversion of coal to liquid fuels involves the gasification of coal to synthesis gas which can be converted to a wide range of hydrocarbons and oxygenates by the well-known Fischer-Tropsch reaction. The catalysts used for the reaction constitute mainly the Group VIII metals such as Ni, Co, Ru, and Fe. The reaction conditions vary in the range of about 1-1000 atm. pressures and 150 - 450° C temperatures. Many review articles on Fischer-Tropsch and related syntheses have been published (1-4).

The major limitation of the conventional Fischer-Tropsch process for converting synthesis gas to gasoline is poor selectivity to the desired products. The products include a wide spectrum of hydrocarbons ranging from methane to waxes and significant amount of oxygenates. The hydrocarbon chain growth in Fischer-Tropsch reactions can be modelled as a polymerization process and the most probable distribution is identical to a Schulz-Flory distribution[5]. This suggests that hydrocarbons in the C_5-C_{11} range for gasoline can be produced at a maximum selectivity of 47 wt% (5,6).

Several approaches have been pursued in an effort to improve the selectivity of the Fischer-Tropsch process depending upon the range of hydrocarbons desired and have been disucssed by King et al.(7).

The discovery of the medium pore zeolite ZSM-5 by Mobil workers has resulted in new routes to Fischer-Tropsch synthesis. The ZSM-5 class of zeolites is active for the conversion of methanol and other oxygenates to hydrocarbons(9). These shape-selective zeolites have high SiO_2/Al_2O_3 ratios (usually greater than 30). The ZSM-5 zeolites have pore openings intermediate between small pore zeolites such as zeolite A and erionite, and large pore zeolites such as faujasites(10).

Recently, Mobil workers have reported a new class of synthesis gas conversion catalysts which produce high-octane gasoline in good yields(11,12). These are bifunctional catalysts comprising a carbon monoxide hydrogenation catalyst with an excess

volume of HZSM-5. Thus, the metal component catalyzes the hydrogenation of CO and the zeolite component catalyzes the conversion of oxygenates and olefins to aromatics.

Mobil investigators have used physical blending of ZSM-5 with a methanol synthesis catalyst(11) or with a Fischer-Tropsch catalyst(12). The bifunctional catalyst can also be prepared by vacuum impregnation of ZSM-5 with metal salt solutions(13,14). For example, Rao et al(13) have used impregnated Fe/ZSM-5 catalyst to produce a liquid hydrocarbon product. The addition of small amounts of cobalt to the Fe/ZSM-5 catalyst was found to suppress the internal shift reaction that is mainly responsible for CO_2 in the product(14). Further characterization studies on Fe/ZSM-5 catalysts have also been reported(15, 16).

It is difficult to achieve uniform distribution of metal on the zeolite surface and pore openings of the zeolite crystals could be blocked by the metal particles. Therefore, other methods of making metal/ZSM-5 catalysts have also been tried(17).

Another variation of Mobil's improved Fischer-Tropsch process is the conversion of synthesis gas to hydrocarbons utilizing dual reactors(18). In this process syngas is converted to C_3^+ product with a CO hydrogenating catalyst (K-Fe) and the product of Fischer-Tropsch synthesis is converted to premium gasoline and distillate fuels in a second reactor containing acidic ZSM-5 zeolite.

The Mobil discovery of bifunctional composite catalysts has resulted in an important approach to controlling product distributions in Fischer-Tropsch synthesis. In general, however, the optimum reaction conditions of operation for each component to the bifunctional catalyst are different. It would be desirable to study the performance of other metal/ZSM-5 systems. In an effort to reduce methane yield and improve the gasoline yield and quality, Mobil's process uses elevated pressures and temperatures, and therefore, it would also be desirable to develop bifunctional catalysts which can make gasoline under milder operating conditions. Furthermore, the elevated pressures may lead to the production of significant amounts of durene (1,2,4,5-tetra-methyl

benzene) in the product(19). Durene has a melting point of 79° C which makes it unsuitable as a gasoline component.

In this work, we have reported the performance of nickel-zirconia, cobalt-nickel/zirconia, and cobalt-nickel/manganese oxide catalyst for CO hydrogenation under mild conditions of temperature and pressure. These Fischer-Tropsch catalysts were studied alone as well as in combination with ZSM-5 in a mixed bed and follow bed arrangements. In addition, the catalysts were characterized by various techniques mentioned in this report.

EXPERIMENTAL

(i) Preparation of Fischer-Tropsch Catalysts

The following 5 zirconia-based catalysts were prepared:

1. 5% Ni/zirconia (called the BASE catalyst and also used as a base for catalysts 2-5)
2. 5% Co on the base
3. 2% Ni - 5% Co on the base
4. 10% Co on the base
5. 3% Co - 6% Ni on the base

A manganese-oxide supported catalyst of following composition was also prepared:

6. 2% Ni - 5% Co/MnO

Catalyst #1 was prepared by the coprecipitation of zirconyl nitrate and nickel nirtrate solutions by excess alkali solution. Thus, 100 g zirconium dinitrate oxide ($Zr(NO_3)_2 \cdot x\ H_2O$ containing 40.2% ZrO_2 from Alfa Products) was dissolved in 200 mL of water, and 10 g nickle nitrate salt ($Ni(NO_3)_2 \cdot 6H_2O$) was dissolved in 200 mL water. The two solutions were mixed and added, drop by drop, with continuous mechanical stirring into 400 mL of 10% NaOH solution under a nitrogen atmosphere. The resulting cake was repeatedly washed with distilled water and filtered (about 10 washes) under N_2 cover protection until the pH of the waste filtrate solution was neutral. This was followed by two washings with acetone and drying in a vacuum oven at 60°C for 24 h. About

38 g of the catalyst thus prepared was ground to pass 200 mesh and stored in a dessicator.

The other four zirconia based catalysts of varying Ni and Co contents (Catalysts No. 2-5) were prepared using the oven-dried Ni/zirconia (#1) (the BASE catalyst) as the support. The impregnation of this support with aqueous solutions of nickel and cobalt salts [$Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$] was carried out by the incipient wetness technique. All the impregnated catalysts were dried in the oven at 100-110°C followed by calcination in a muffle furnace at 500°C for 24 h.

Catalyst #6 was prepared by impregnation of granular manganese oxide of size range -100+200 mesh with aqueous solution of metal salts. The impregnation was carried out by the incipient wetness technique. The starting materials were $Ni(NO_3)_2 \cdot 6H_2O$ from Matheson Coleman & Bell, $Co(NO_3)_2 \cdot 6H_2O$ from B.D.H. and manganese oxide (99.5% MnO) from Alfa Products. The impregnated catalyst was dried in an oven at 100-110°C. The catalyst was calcined in a muffle furnace for 24 h at 500°C.

(ii) Preparation of Zeolite Catalyst ZSM-5

ZSM-5 catalyst was prepared in the laboratory according to the method reported in the patent literature (20). The procedure involved the heating of a mixture containing appropriate amounts of sodium silicate solution, aluminum sulfate, propanol and ZSM-5 seed slurry in an autoclave at 175°C for 1-4 days. This was followed by filtering, washing, and calcinating of the resulting product. The H^+ form was made by acid leaching using HCl. A crystallization time of 24 h was chosen as the optimum, based on the x-ray analysis of various samples. The details of the procedure for preparation of ZSM-5 are given in Appendix A.

(iii) Characterization of Catalysts

The Fischer-Tropsch catalysts were characterized by BET surface area, atomic absorption and temperature-programmed reduction. The results of atomic absorption analyses and surface area measurements are given in Table 1. The details and procedure

used for temperature programmed reduction (TPR) are described in Ref. 21. For TPR studies, a mixture of 3.1% hydrogen in nitrogen was used as carrier gas. Its flow rate was 30 mL/min. A weighed sample of catalyst (about 0.1 g) was contained in a quartz U-tube reactor heated from 298 K to 973 K at a rate of 6 K/min with the help of a linear temperature programmer. The hydrogen uptake, monitored by a thermal conductivity detector, as a function of temperature was recorded by a two-pen recorder. The TPR profiles thus obtained are shown in Figs 1-3.

The zeolite ZSM-5 was characterised by x-ray diffraction, atomic absorption, and Constraint Index (C.I.) determination. The x-ray diffraction pattern of the sample was identical to that reportd in Ref. 8. It indicates that the sample was completely crystalline ZSM-5. The atomic absorption analysis of the sample showed 0.14% Na (by weight), and SiO_2 to Al_2O_3 weight ratios of 34.3. The importance and method of measurement of C.I. has been given in Ref. 18. Briefly, the C.I. directly gives the information about the necessary constrained access existing in the zeolite to the desirable molecules, which sometimes can also be judged from the known crystal structure of the zeolite. The C.I. value for our zeolite sample was determined as 8.0. The detailed procedure and calculations are given in Appendix B.

(iv) Apparatus and Procedure for Syngas Conversion

Synthesis gas conversion tests were carried out at atmospheric pressure in a down-flow stainless-steel microreactor of 0.44 cm i.d. (see Figure 1). The reactor was surrounded by a metal block heater whose temperature was controlled to $\pm$ 1° C. The premixed synthesis gas mixture (used as feed) contained 10-20% argon which served as an internal standard in product analysis by gas chromatography. Two feed gas compositions were used:

1. 42.1% CO, 38.7% H_2, 19.2% Ar (H_2/CO = 0.92)
2. 30% CO, 60% H_2, 10% Ar (H_2/CO = 2)

The screening tests carried out in this investigation can be catagorised as follows:

1. Screening of Fischer-Tropsch (FT) catalysts alone
2. Screening of FT catalysts combined with HZSM-5

Further, the combined FT + HZSM-5 tests (category 2) were carried out using two types of bed arrangements.

(a) Follow Bed Arrangement: In this arrangement, the synthesis gas mixture passed through the bed of FT catalyst followed by that of HZSM-5. The two beds were separated by quartz wool.

(b) Mixed Bed Arrangement: In this arragement, the FT catalyst was physically mixed with HZSM-5 and then the mixture was loaded into the reactor.

The catalyst was pretreated in-situ under flowing hydrogen (30 mL/min) at 450°C for 16 hours. The catalyst temperature was lowered to the reaction temperature before introducing the feed gas.

The reaction products were analyzed using on-line gas chromatographs equipped with following columns:

1. 3% OV-101 on WHP 80/100 and 10% T.C.E.P. on chromosorb PAW - for C_6 and higher hydrocarbons including detailed aromatics distribution.
2. Chromosorb 102 and 0.19% picric acid on Carbopac C - for C_1-C_5 hydrocarbons.
3. Carbosieve S-for Ar, CO and CO_2.

The calibration was carried out using various calibration mixtures and pure compounds.

RESULTS AND DISCUSSION

Some of the physico-chemical properties of the catalysts are summarised in Table 1.

(i) Testing of Fischer-Tropsch Catalysts

The operating conditions and product distribution for 5% Ni/zirconia (catalyst #1) at three different reaction temperatures are given in Table 2. It is seen that increasing the temperature increases the methane percent and decreases the C_5^+ fraction in the product. Higher temperatures of 300° C and above also cause fast deterioration of the catalyst.

The product selectivity data for zirconia based catalysts are summarized in Tables 3-4. Table 3 shows the hydrocarbon selectivity for the catalysts at two different H_2/CO ratios, at 250°C, and 1 atm pressure. It is seen that an increase in H_2/CO ratio increases the methane wt% in the product for all the catalysts to varying extent. Table 4 shows the selectivity to olefins in the C_2, C_3, and C_4 molecular weight fractions, at 250° C, 1 atm., H_2/CO = 0.92 and approximately 5% conversion in each case. The ratio $C_2^=/C_2$ is generally a function of conversion and H_2/CO ratios. Higher conversions and higher H_2/CO ratios give somewhat lower olefin selectivity. The ratio $C_3^=/C_3$ is only weakly dependent on process variables except for a tendency to decrease with increasing H_2/CO. The ratio $i\text{-}C_4/C_4$ is nearly independent of temperature and decreases slightly with both increasing conversion and increasing H_2/CO ratio.

The operating conditions and product distribution for 2% Ni - 5% Co/MnO catalyst (#6) are given in Table 5. Table 5 shows a trend similar to zirconia based catalyst (#1, Table 2), i.e. an increase in temperature results in an increase in methane wt% in the product.

(ii) Testing of Fischer-Tropsch Catalysts Combined with HZSM-5

The operating conditions and product analysis for a typical run in the follow bed arrangement using 10% Co/zirconia base catalyst as an FT component are reported in Table 6. It is seen that the presence of HZSM-5 results in the formation of aromatics which are not formed when Fischer-Trospch Catalyst is used alone (i.e. without HZSM-5). It was observed that during the initial period of starting the run, the percentage of aromatics increased with time-on-stream and the steady-state product distribution (such as reported in Table 6) was reached after about 5-10 h of continuous operation.

Table 7 presents typical steady-state product distributions for 10% Co/zirconia base catalyst under nearly similar operating conditions but varying HZSM-5/FT weight ratios. It is seen that

percentage aromatics increases from 8.4% to 22.5% by increasing the weight ratios of HZSM-5/FT ratio from 1 to 4. However, the aromatics content almost reaches a plateau at HZSM-5/FT ratios of 4. Based on this observation, further experiments were carried out at HZSM/FT ratio of 4.

It was observed that an increase in H_2/CO ratio results in decrease in aromatics. Increasing the temperature slightly increases the aromatics but also results in an increase in methane percent and faster deactivation of Fischer-Tropsch catalyst. Therefore, most of the experiments were carried out in the temperature range of 250 - 260°C and at H_2/CO ratio of 0.92.

Typical product distributions obtained using 5% Ni-ZrO_2 (the base catalyst) alone and combined with HZSM-5 in follow bed and mixed bed modes are compared in Table 8. It is seen that the presence of HZSM-5 causes a substantial decrease in methane selectivity, lowers the olefin/paraffin ratio (as shown for C_2 and C_3 fractions), markedly increases the selectivity of C_4 fraction and gives excellent yields of the desired aromatics. The weight percent of aromatics in the product mixture from follow and mixed bed arrangements are comparable. However, the olefinicity of C_2 and C_3 fractions is higher in mixed bed than in the follow bed. In addition, it is observed that the decrease in the olefinicity of C_3 fraction (from FT products alone to mixed or follow bed operations) is more severe as compared to the olefinicity of C_2 fraction. Similar effects are observed when 5% Co/zirconia base catalyst issued as an FT component (Table 9). A comparison of Tables 8 and 9 suggests that the impregnation of cobalt on zirconia base does not produce any measurable change in aromatic content but results in increased content of C_5^+ fraction as well as the olefin content of the C_2 and C_3 fractions.

Table 10 gives the results of hydrocarbon analyses when 2% Ni - 5% Co/MnO is used as an FT catalyst alone as well as combined with HZSM-5. It is observed that the effects of combining with HZSM-5 are similar to those described above for zirconia based catalysts (Tables 8 and 9). However, a comparison of the results for 2% Ni - 5% Co/MnO catalyst with those reported for zirconia

based catalysts suggests that the use of 2% Ni - 5% Co/MnO catalyst as an FT component produces higher amount of methane and lower amounts of C_5^+ and aromatics. Therefore, zirconia based catalysts are superior to manganese oxide supported catalyst for the reaction of our interest.

A comparison of product distributions for all the five zirconia based catalysts, both in follow bed as well as mixed bed arrangements is reported in Tables 11 and 12, respectively. It is seen that under favourable conditions of operation, all the Fischer-Tropsch (FT) catalysts exhibit low methane formation and high selectivity to aromatics. This desirable product distribution is believed to be due to highly olefinic products obtained from the FT component of the catalyst system. However, the 5% Ni - ZrO_2 system (FT Cat. #1) gives relatively lower yields of C_5^+ fraction, compared to other four catalyst preparations. This trend is observed in both the follow bed (Table 11) as well as in mixed bed operation (Table 12). On this basis, 5% Ni-ZrO_2 system (FT Cat #1) should be dropped in preference to the other four catalysts. Among the rest of the catalysts (# 2-5), 2% Ni - 5% Co/Base gave the highest selectivity to aromatics and lowest methane selectivity in the follow bed operation (Table 11). The highest selectivity to aromatics using 2% Ni - 5% Co/Base was observed in the mixed bed operation as well (Table 12). In view of maximum aromatics and low methane contents in the products, 2% Ni - 5% Co/Base appears to be a probable choice among the four impregnated catalysts for further detailed studies. However, it must be emphasized that the task of picking out a catalyst is made more difficult by the excellent aromatics selectivity and low methane selectivity given by all the zirconia based catalysts studied in this investigation. For example, the catalyst 10% Co/Base also appears to be equally promising in terms of activity and selectivity toward C_5^+ fraction and aromatics. It has been observed that the key to obtaining the desired products is the control of operating conditions within a narrow range. We believe, further testing of a chosen catalyst under various operating conditions will give more insight into the effect of

operating conditions and thus help in finding the optimum conditions of operation.

Based on the above results and discussion, it is planned to use 2% Ni - 5% Co/Base and 10% Co/Base systems as Fischer-Tropsch catalysts for further investigations.

SUMMARY AND CONCLUSIONS

Synthesis gas conversion reaction was carried out using an isothermal 1/4" OD micro reactor. Six Fischer-Tropsch (FT) catalysts were prepared and characterised by TPR, BET surface area, atomic absorption etc. Five of the Fischer-Tropsch catalysts were nickel-zirconia and nickle-cobalt-zirconia preparations with varying Co/Ni ratios. The sixth catalyst was manganase oxide supported nickel-cobalt. ZSM-5 zeolite catalyst was prepared and characterised by BET surface area, atomic absorption, X-ray diffraction, and constraint index determination.

The FT catalysts were tested for activity and selectivity for CO hydrogenation alone as well combined with HZSM-5 under mild reaction conditions. The results obtained in this work are extremely encouraging in as much as high yields of aromatic rich C_5^+ products are obtained with low methane selectivities. However, it requires large bed lengths of HZSM-5 (HZSM-5/FT ratio of 4). We believe that the amount of HZSM-5 can be reduced by operating the HZSM-5 catalyst at higher temperature. In the follow bed arrangement or in mixed bed arrangement, increase in temperature above 250 - 260^{o}C is not desirable owing to the limitations in the operating conditons of FT component. It is therefore, highly recommended that a dual bed arrangement equipped with independent temperature control for FT and HZSM-5 catalysts be tried in order to further optimize the production of the desired products.

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APPENDIX A

Preparation of ZSM-5 Catalyst

Materials

1. Sodium Silicate (commercial solution)
   Fischer Scientific 40-42° Be, Technical Analysis:

%Na_2O	11.8
%SiO_2	29.8
%H_2O	58.4

2. n-Propanol, Certified, Fischer Scientific
3. Aluminum Sulfate crystals, Certified $Al_2(SO_4)_3 \cdot 18H_2O$. Fischer Scientific.
4. Seed slurry containing crushed ZSM-5 particles.

Procedure

Take (A) 66 g Sodium Silicate Solution
(A) 7.5 g n-propanol
(B) Aluminum sulfate solution containing
4.6 g $Al_2(SO_4)_3 \cdot 18H_2O$
4.8 g H_2SO_4
114.0 g H_2O
(A) 84 g seed slurry (containing 100 mg crushed ZSM-5 particles 0.2 mm in size in water.

Mix solutions (A) and (B) thoroughly with blender to break up the gel until homogeneous. Heat with stirring (in an autoclave) at 175° C for 24 h. Filter off crystals, wash thoroughly with hot distilled water, dry at 110° C, calcine at 550° C. To produce H^+ form for catalysis, acid leach refluxing 0.5 molar HCl for 16 hours. Wash with water. Calcine at 400° C in air for 4 h.

APPENDIX B

Estimation of Constraint Index

The C.I. was determined in our experiments using the following procedure. The zeolite powder was air-calcined at 500° C for 2 h. The pellets were made by a tablet machine which were crushed and sieved to give particle size of 0.028 - 0.05 in. A weighed amount of zeolite (0.2 g) was loaded into the microreactor. Helium was passed through the zeolite and the reactor temerature was raised to 300° C. Then a mixture of equal weight of n-hexane and 3-methyl pentane was passed continuously with helium dilution. After 20 minutes on stream, a sample of the effluent was analyzed by gas chromatography using 10% OV-101 column to determine the fraction remaining unchanged for each of the two hydrocarbons.

The "Constraint Index" is calculated as follows:

$$\text{Constraint Index (C.I.)} = \frac{\log_{10}(\text{fraction of n-hexane remaining})}{\log_{10}(\text{fraction of 3-methyl pentane remaining})}$$

The experiments for determination of the C.I. were carried out in the microreactor apparatus with minior modifications. The hydrocarbon mixture with helium dilution was made by continuously passing helium through a bubbler containing the mixture of liquid hydrocarbons at room temperature. The helium was passed through the bubbler for about one hour to attain equilibrium state before the stream was diverted to the reactor. It was realized that the weight ratio of two hydrocarbons (n-hexane) and (3-methyl pentane) in the helium stream exiting the bubbler would be different from the ratio of the two liquid hydrocarbons within the bubbler due to difference in volatilities (or boiling points) of the two hydrocarbons. By trial runs, it was found that the bubbler liquid containing about 27 wt% 3-methyl pentane and the rest n-hexane gave approximately equal weight ratios of hydrocarbons in exiting stream after about 1 hour of continuously passing helium.

The operating conditions and results of a typical experiment for C.I. determination are given below:

Weight of HZSM = 0.2 g
Volumetric flow rate of liquid hydrocarbons = 0.63 mL/h
Bulk Volume of catalyst in the reactor = 1.4 mL
Flow rate of helium = 8.73 mL/min = 0.022 moles/h
Liquid hourly space velocity = 0.63/1.4 = 0.45
Mole ratio helium/total hydrocarbons = 4.49
Fraction of n-hexane unconverted = 0.295
Fraction of 3-methyl pentane unconverted = 0.858

$$\text{Constraint Index} = \frac{\log_{10}(0.295)}{\log_{10}(0.858)} = 8.0$$

This value of C.I. matches very well with the value of 8.3 reported for ZSM-5 catalyst in the Ref. 18. This indicates that the zeolite made in this laboratory is suitable for catalyzing the reaction of our interest.

Table 1. Physico-chemical characteristics of various catalysts

No.	Catalyst*	Average Particulate size[a], μm	BET surface area m^2/g	Bulk density** g/cc	Metal Analysis wt% Ni	Co
1	5% Ni-ZrO_2	1.2	105	0.6	4.9	-
2	5% Co/Base	6.3	65	0.6	4.4	6.0
3	2% Ni-5% Co/Base	6.2	78	0.1	6.6	5.8
4	10% Co/Base	10.2	75	0.7	3.2	8.8
5	3% Co-6% Ni/Base	3.5	89	0.7	8.2	2.6
6	2% Ni-5% Co/MnO	282	5	1.82	1.4	3.3
-	HZSM-5[b]	6.7	362	0.2	-	-

*Catalysts 1-6 calcined in muffle furnace at 500°C for 24 h; HZSM-5 calcined at 400°C.

**As determined by volume occupied in a 1/4" OD glass tube.

a. As determined by optical microscope

b. Na = 0.14%, Al = 1.5%. This corresponds to SiO_2/Al_2O_2 weight ratio of 34.3, and molar ratio of 58.4.

Table 2. Fischer-Tropsch reaction over 5% Ni/zirconia catalyst - Effect of temperature on product distribution.

Run No.	134	136	138
Wt. of Catalyst, g	0.2992	0.2992	0.2992
Exit Flow Rate, mL/min	15.0	16.1	15.5
Reactor Temperature, ^{o}C	250	275	300
CO Conversion %	5.0	7.9	7.4
Hydrocarbon Analysis, wt%			
C_1	27.4	37.1	52.7
C_2	20.6	20.0	19.0
C_3	20.7	17.3	13.6
C_4	10.9	8.5	5.6
C_5	6.7	5.2	2.9
C_6	4.2	3.3	1.7
C_7	2.9	2.4	1.1
C_8	1.8	1.7	0.8
C_9	1.0	0.8	0.3
C_{10}	0.8	0.7	0.1
C_{11}	0.4	0.9	0.2
C_{12}	0.6	0.7	0.1
C_{13}	1.1	0.8	1.0
C_{14}	0.5	0.6	0.2
C_{15}	0.5	0.1	-
C_5^+	20.4	17.2	8.4
$C_2^=$/Total C_2, wt%	45	42	30
$C_3^=$/Total C_3, wt%	87	88	81

Feed: 19.2% Ar, 42.1% CO, 38.7% H_2

Table 3. Product distributions for zirconia based catalysts*

Catlayst No.	Nominal Catalyst	Co/Ni (Based on AA Analysis)	H_2/CO = 0.92 Selectivity, wt%					H_2/CO = 2.0 Selectivity, wt%				
			C_1	C_2	C_3	C_4	C_5^+	C_1	C_2	C_3	C_4	C_5^+
1	5% Ni-ZrO_2	0	27	20	21	11	21	36	21	18	9	16
5	3% Co, 6% Ni on Base	0.3	12	6	12	10	60	16	10	13	10	51
3	5% Co, 2% Ni on Base	0.9	17	5	13	11	54					
2	5% Co on Base	1.4	15	5	11	11	58	19	5	12	11	53
4	10% Co on Base	2.8	15	4	9	8	64	17	4	8	8	63

* Temperature 250°C, Pressure 1 atm.

Table 4. Product selectivity (-enes/total) for zirconia-based catalyst*

Cat. No.	Co/Ni	Selectivity, wt%		
		$C_2^=$/Total C_2, wt%	$C_3^=$/Total C_3, wt%	i-C_4/Total C_4, wt%
1	0	45	87	51
3	0.9	39	87	60
2	1.4	47	89	60
4	2.8	57	91	72

Table 5. Fischer-Tropsch reaction over 2% Ni-5% Co/MnO catalyst-effect of reaction temperature on product distribution.

Run No.	370	371	373	375
Wt. of Catalyst, g	0.2	0.2	0.2	0.2
Exit Flow Rate, mL/min	2.5	2.5	2.5	2.5
Time-on-stream, h	21.2	23.0	26.0	46.5
Reactor Temperature, ^{o}C	250	260	275	300
CO Conversion, %	11.8	12.1	14.7	16.5
Hydrocarbon Analysis, wt%				
C_1	28.4	32.7	42.1	57.9
C_2	5.8	6.2	7.1	7.5
C_3	11.1	11.7	12.4	9.4
C_4	9.8	9.8	9.5	5.8
C_5	8.8	8.3	7.5	4.1
C_6	7.6	6.9	5.6	3.1
C_7	5.9	5.2	4.2	2.1
C_8	4.8	4.1	3.3	1.7
C_9	3.7	3.0	2.2	1.2
C_{10}	2.8	2.0	1.3	0.8
C_{11}	2.4	1.8	1.1	0.7
C_{12}	2.5	1.9	1.2	0.7
C_{13}	2.4	1.9	1.0	1.1
C_{14}	2.0	2.2	0.7	1.7
C_{15}	2.2	2.3	0.9	2.1
C_5^+	45.0	39.6	28.9	19.5
$C_2^=$/Total C_2, wt%	29	28	31	60
$C_3^=$/Total C_3, wt%	84	83	82	91

Feed 19.2% Ar, 42.1% CO, rest H_2

Table 6. Detailed product distribution using 10% Co/Base combined with HZSM-5 in follow bed arrangement.

Wt. of FT Cat: 0.1 g

Wt. of HZSM-5: 0.15 g

Feed Composition: 19.2% Ar, 42.1% CO, rest H_2

Exit Flow Rate: 8.8 mL/min

Reactor Temperature: 275°C

Reactor Inlet Pressure: 3.5 psig

CO Conversion: 10.5%

Hydrocarbon Analysis, wt%

C_1	29.7
C_2	3.8 (olefin/paraffin = 1.0)
C_3	10.8 (olefin/paraffin = 0.5)
C_4	22.7
C_5+	12.9
Aromatics (A_6-A_9)	20.1
	100.0

Detailed composition of Aromatics:

A_6	2.7
A_7	21.4
A_8	44.9
A_9	31.0
	100.0

Detailed composition of C_4 Fraction:

Isobutane	57.9
1-butene	1.5
n-butane	21.7
Isobutylene	10.9
cis-2-butene	2.8
trans-2-butene	4.5
1,3-butadiene	0.6
	100.0

Table 7. Typical product distributions at varying HZSM-5/FT weight ratios*

HZSM-5/FT ratio	1	3	4
Wt. of FT, g	0.1	0.1	0.075
Wt. of HZSM-5, g	0.1	0.3	0.3
Flow rate, mL/min.	9.4	7.9	8.2
Reactor Temperature, ^{o}C	250	250	250
Time-on-stream, h (approx.)	6	5	5
Hydrocarbon analysis, wt%			
C_1	13	11.9	13.9
C_2	2.7	2.5	2.5
C_3	10.5	9.3	9.7
C_4	24.2	19.9	24
C_5^+ (excluding aromatics)	41.3	34.5	27.5
Aromatics	8.4	22	22.5

*FT catalyst 10% Co/Base; feed composition 19.2% Ar, 42.1% CO, rest H_2, follow bed arrangement.

Table 8. Typical product distribution for the Base catalyst alone and in combination with HZSM-5.

Run No.		134	247	281
Wt. of FT Cat. g		0.2992	0.075	0.075
Wt. of HZSM-5, g		0.0	0.3	0.3
Exit flow rate,mL/min.		15.0	3.6	4.0
Bed Arrangement		FT Catalyst only	Follow Bed	Mixed Bed
Hydrocarbon Analyst, wt%				
Aliphatics:	C_1	27.4	17.1	19.6
	C_2	20.6	9.9	7.0
	C_3	20.7	9.9	7.7
	C_4	10.9	15.8	18.0
	C_5^+	20.4	15.5	18.4
Aromatics:	A_6	0.0	0.3	0.3
	A_7	0.0	4.5	3.6
	A_8	0.0	10.4	8.6
	A_9	0.0	10.2	11.2
	A_{10}^+	0.0	6.3	5.6
Total Aromatics		0.0	31.7	29.3
C_2=/Total C_2,wt%		45	3	20
C_3=/Total C_3, wt%		87	2	16

Temperature, 250°C, Feed 19.2% Ar, 42.1% CO, rest H_2.

Table 9. Typical product distribution for the 5% Co/Base FT Catalyst alone and in combination with HZSM-5

Run No.		242	232	291
Wt. of FT Cat., g		0.075	0.075	0.075
Wt.of HZSM-5, g		0.0	0.30	0.30
Exit flowrate mL/min		4.2	4.0	3.8
Bed Arrangement		FT Cat. only	Follow Bed	Mixed Bed
Hydrocarbon Analysis, wt%				
Aliphatics	C_1	21.7	16.6	15.7
	C_2	5.8	2.2	2.2
	C_3	11.4	9.9	8.2
	C_4	10.3	22.9	21.5
	C_5^+	50.7	22.7	23.5
Aromatics	A_6	0.0	0.5	0.4
	A_7	0.0	5.2	4.2
	A_8	0.0	8.7	9.7
	A_9	0.0	3.9	9.0
	A_{10}^+	0.0	7.4	5.6
Total Aromatics		0.0	25.7	28.9
C_2=/Total C_2, wt%		57	17	39
C_3=/Total C_3, wt%		93	4	20

Temperature 250°C, Feed 19.2% Ar, 42.1% CO, rest H_2.

Table 10. Typical product distribution for 2% Ni-5% Co/MnO FT Catalyst alone and in combination with HZSM-5.

Run No.		370	348	361
Wt. of FT Cat., g		0.2	0.20	0.199
Wt. of HZSM-5, g		0.0	0.2001	0.2003
Exit flow rate, mL/min.		2.5	3.3	2.8
Bed Arrangement		FT Cat. only	Follow Bed	Mixed Bed
CO Conversion %		11.8	3.8	7.0
Time-on-stream, h		21.2	22	23
Hydrocarbon Analysis, wt%				
Aliphatics	C_1	28.4	27.4	27.8
	C_2	6.0	5.5	5.0
	C_3	11.1	9.8	8.3
	C_4	9.8	22.8	21.4
	C_5^+	45.0	17.5	19.5
Aromatics	A_6	0.0	0.5	0.4
	A_7	0.0	5.0	3.7
	A_8	0.0	6.6	6.8
	A_9	0.0	2.5	4.1
	A_{10}^+	0.0	2.8	3.3
Total Aromatics		0.0	17.1	18.1
$C_2^=$/Total C_2, wt%		30	17	23
$C_3^=$/Total C_3, wt%		84	0	30

Temperature 250°C, Feed 19.2% Ar, 42.1% CO, rest H_2.

Table 11. Comparison of Product Distributions in a Follow Bed Operation Using Various FT Catalysts.

Run No.		247	232	260	222	268
Wt. of FT Cat., g		0.075	0.075	0.0753	0.075	0.0751
Wt. of HZSM-5, g		0.30	0.30	0.3004	0.3	0.3004
Exit Flow Rate, mL/min		3.6	4.0	3.8	3.9	3.6
FT Cat.		5% Ni/ZrO_2	5% Co/Base	2% Ni-5%Co / Base	10%CO/Base	3%CO+6%Ni / Base
		#1	#2	#3	#4	#5
CO Conv. %		13.8	7.2	10.8	13.0	12.1
Time-on-stream, h		21	22.5	24.3	23.5	23.5
Hydrocarbon Analysis, wt%						
Aliphatics	C_1	17.1	16.6	12.3	16.3	19.3
	C_2	9.9	2.2	2.2	2.0	6.0
	C_3	9.9	9.9	8.7	9.8	9.1
	C_4	15.8	22.9	20.0	21.3	17.8
	C_5^+	15.5	22.7	22.2	23.0	19.2
Aromatics	A_6	0.3	0.46	0.4	0.4	0.4
	A_7	4.5	5.2	5.3	4.3	4.8
	A_8	10.4	8.7	12.0	10.1	10.1
	A_9	10.2	3.9	10.4	7.3	5.6
	A_{10}^+	6.3	7.4	6.5	5.5	5.6
Total Aromatics		31.7	25.7	34.7	27.6	28.5
$C_2^=$/Total C_2, wt%		3	17	14	20	4.1
$C_3^=$/Total C_3, wt%		2	4	3	4.7	4.1

Temperature 250°C, Feed: 19.2% Ar, 42/1% CO, rest H_2.

Table 12. Comparison of product distribution in a mixed bed operation using various FT catalysts.

Run No.		281	291	303	315	327
Wt. of FT Cat., g		0.075	0.075	0.0752	0.0752	0.0752
Wt. of HZSM-5, g		0.30	0.30	0.30	0.3003	0.3004
Exit Flow Rate, mL/min		4.0	3.8	4.5	4.0	4.0
FT Cat.		5%Ni/ZrO_2	5%Co/Base	2%Ni-5%Co/Base	10%CO/Base	3%Co+6%Ni/Base
		#1	#2	#3	#4	#5
CO Conv. %		8.9	7.4	9.2	12.9	12.2
Time-on-stream, h		23.5	22.5	26	23.5	23.5
Hydrocarbon Analysis wt%						
Aliphatics	C_1	19.6	15.7	17.0	18.1	16.4
	C_2	7.0	2.2	2.5	2.1	3.4
	C_3	7.7	8.2	8.9	8.1	8.5
	C_4	18.0	21.5	20.7	21.3	21.0
	C_5^+	18.4	23.5	21.5	25.0	23.2
Aromatics	A_6	0.3	0.4	0.4	0.4	0.4
	A_7	3.6	4.2	4.6	3.7	3.9
	A_8	8.6	9.7	10.1	8.9	9.5
	A_9	11.2	9.0	9.2	8.2	8.9
	A_{10}^+	5.6	5.6	5.0	4.4	4.9
Total Aromatics		29.3	28.9	29.4	25.5	27.5
C_2=/Total C_2, wt%		20	39	40	45	24
C_3=/Total C_3, wt%		16	20	18	23	15

Temperature 250°C, Feed: 19.2% Ar, 42.1% Co, rest H_2.

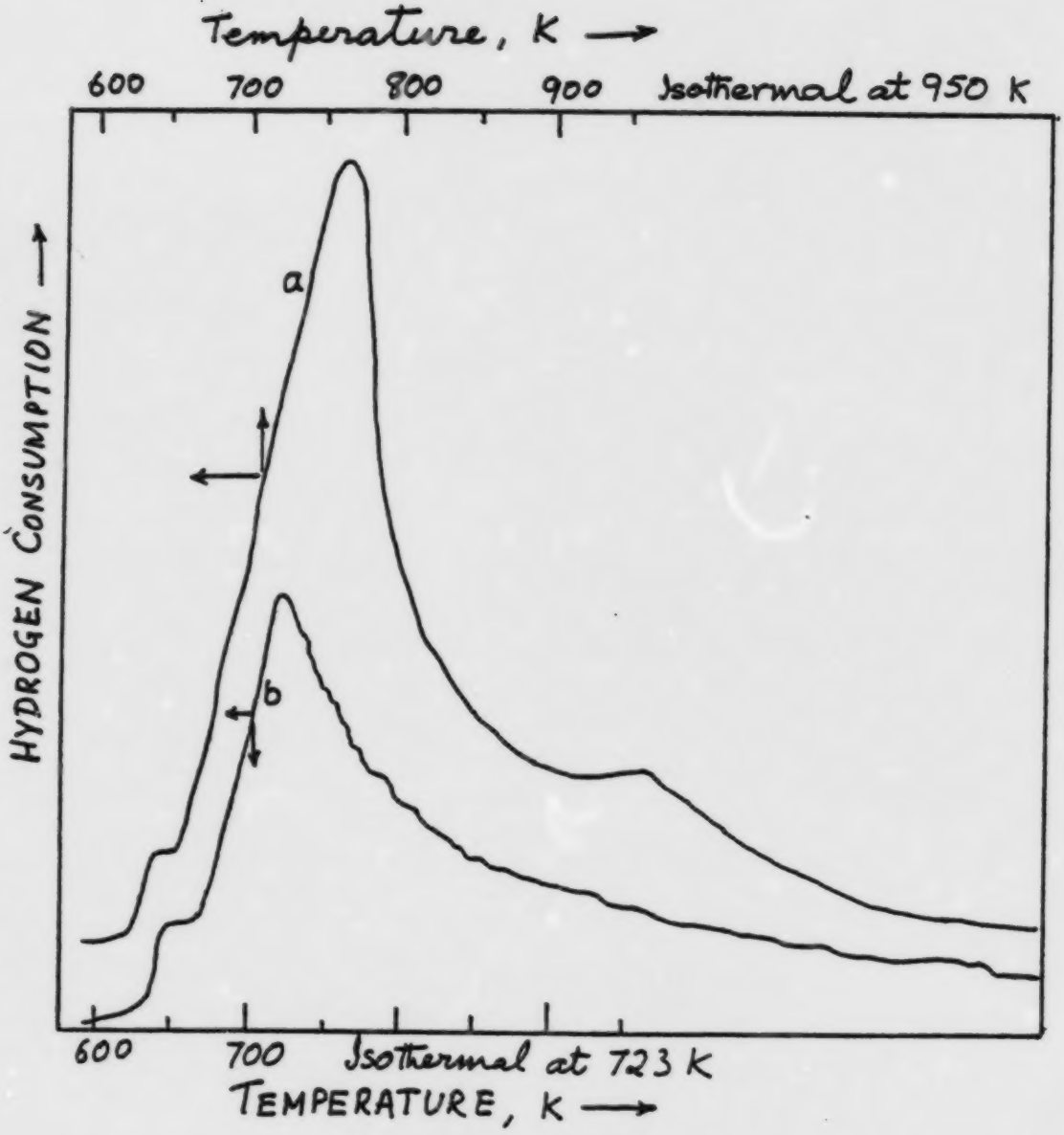

Fig. 1. TPR Profile of 5%Ni-Zirconia. a. temperature programmed upto 950 K and maintained isothermal at 950 K; b. temperature programmed upto 723 K and maintained isothermal at 723 K overnight.

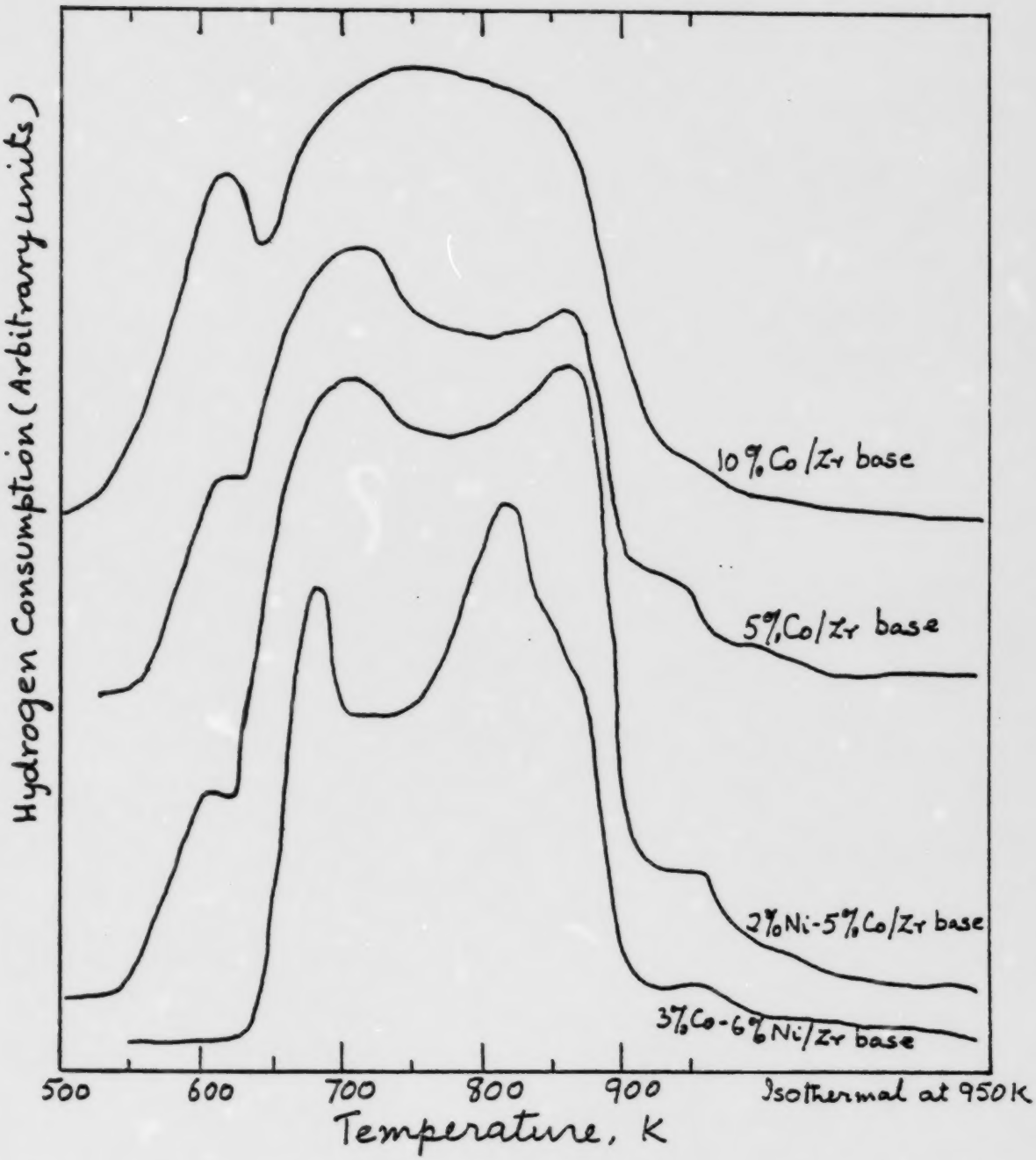

Fig. 2. TPR profiles of nickel-cobalt/zirconia catalysts.

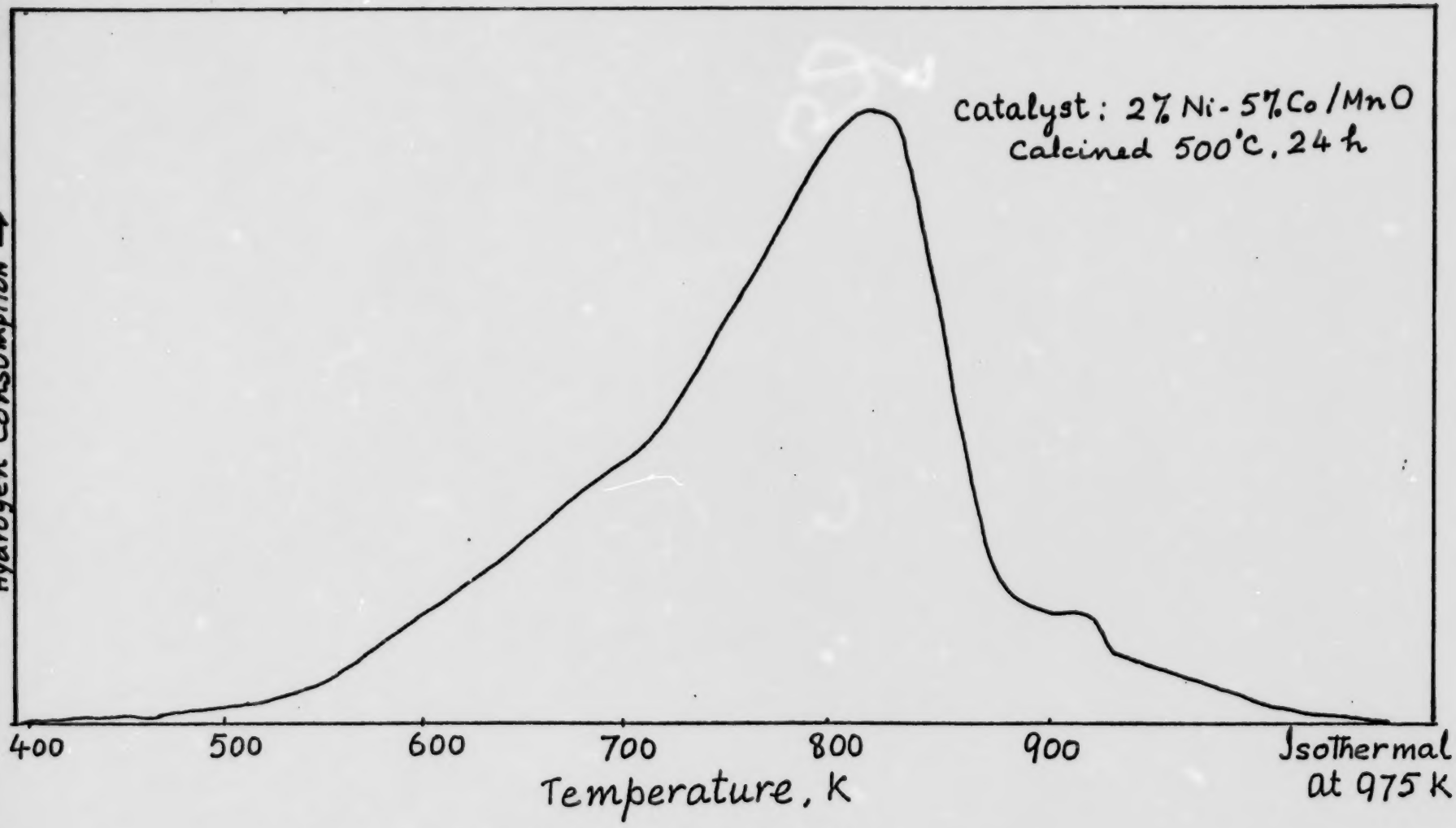

Fig. 3. TPR Profile of Ni-Co/MnO catalyst.

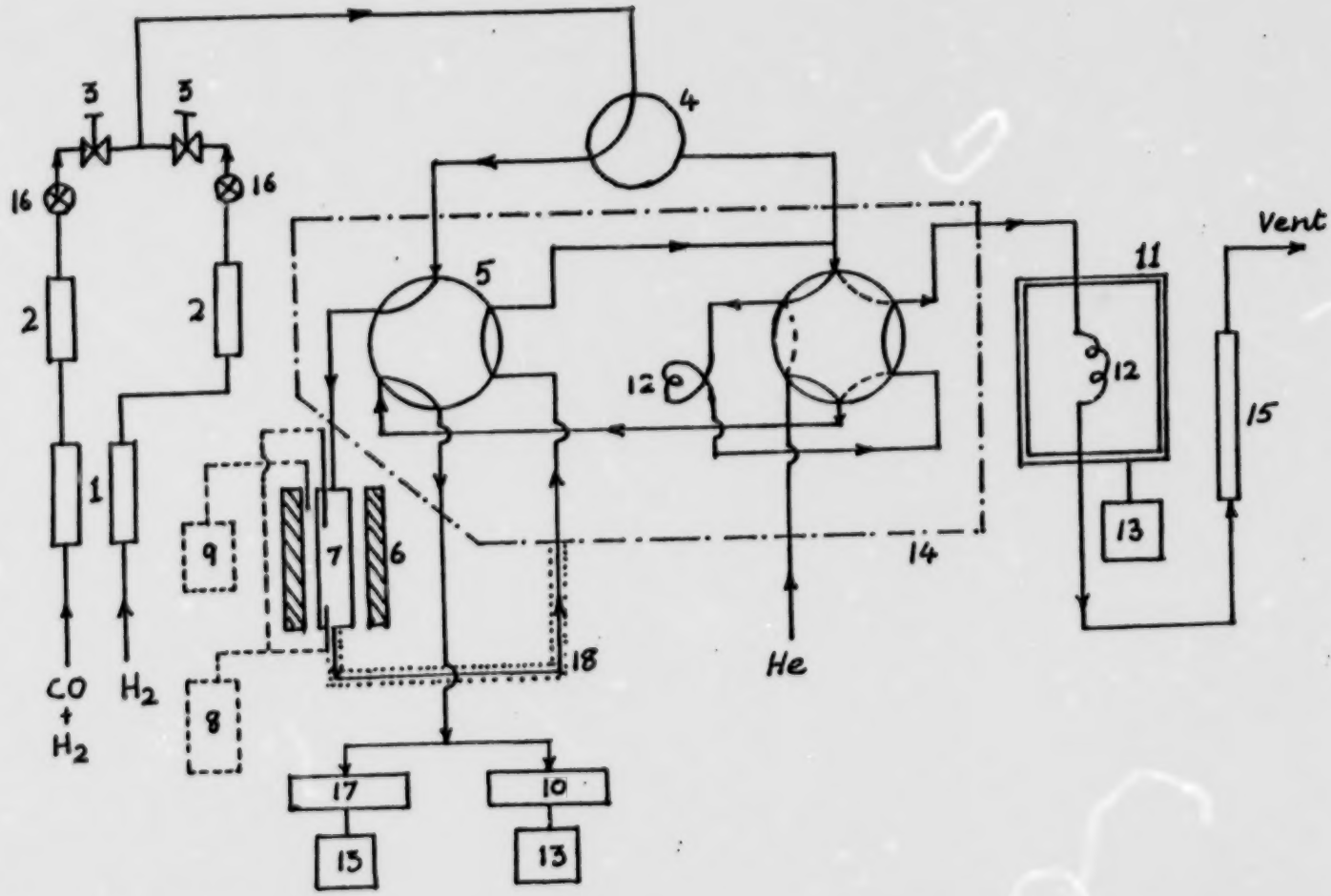

Fig. 4. Apparatus for carbon monoxide hydrogenation (1) gas purifier (2) flow meter (3) needle valve (4) three-way valve (5) six-way valve (6) furnace (7) reactor and preheater assembly (8) multi-channel temperature indicator (9) temperature controller-indicator(10) gas chromatograph FID (11) gas chromatograph-FID (12) sample loop (13) integrator (14) heating chamber (15) bubble flow meter (16) shut-off valves (17) gas chromatograph - TCD (18) heated reactor exit line.

Summary of FT Experiments

Run No	Cat.	Ranges of Operating Conditions: Temp°C	Feed	Cat wt g	Flow rates mL/min
106-126	2%Ni-5% Co/MnO	250-300	CO/H_2=1 CO/H_2=0.5	0.514	2.9-23
127-138	Base	250-300	"	0.299	10.2-16.6
139-148	2%Ni-5%Co/Base	250-300	"	0.1193	9.6-19.2
149-155	5%Co/Base	250-300	"	0.1	10.2-17.6
156-163	10%Co/Base	240-275	"	0.0929	9.2-18.8
164-171	3%Co+6%Ni/Base	240-275	"	0.0947	8.9-19.2
335-344	2%Ni-5%Co/MnO	250-300	"	0.1	3.6-11.3
368-376	2%Ni-5%Co/MnO	250-300	"	0.2	2.5-2.6

Analysis of a Typical Run

CO Conv %	Typical run no.	Operating Conditions: Temp °C	Feed CO/H_2	Cat wt g	Flow rate ml./min	H.C. Analysis, wt% C_1	C_2	C_3	C_4	C_5^+
4.2	106	300	1.0	0.514	21.4	61.7	12.0	13.9	6.7	5.7 (analyzed up to C_6 only)
5.0	134	250	1.0	0.299	15	27.4	20.6	20.7	10.9	20.4
10.4	139	250	1.0	0.1193	9.2	18.1	5.7	13.0	11.4	51.8
10.4	150	250	1.0	0.1	10.2	15.7	4.7	11.5	10.5	58.0
8.8	157	250	1.0	0.0929	9.2	14.6	3.9	9.6	9.0	62.9
14.2	165	250	1.0	0.0947	8.9	12.1	6.2	12.6	10.1	59.0
	The results might be inaccurate due to very low conversion. The runs were repeated using higher amount of catalyst.									
11.8	370	250	1.0	0.2	2.5	28.3	5.8	11.0	9.8	44.9

Summary of FT + HZSM-5 Experiments (Mixed Bed Arrangement)

Run No.	FT Catalyst	Ranges of Operating Contions					Analysis of a Typical Run, wt%											
							Operating Conditions											
		Temp °C	Feed CO/H_2	FT Cat. g	HZSM-5 g	Exit Flow rates ml/min	CO Conv %	Typical Run No.	Temp °C	Feed CO/H_2	FT Cat Wt, g	HZSM-5 g	Exit flow rate mL/min	C_1	C_2	C_3	C_4	C_5^+ Aliphatics	Total Aromatics
278-287	5%Ni/ zirconia	250-260	1.0	0.075	0.3	4.0-9.9	8.9	281	250	1.0	0.075	0.3	4.0	19.6	7.0	7.7	18.0	18.4	29.3
288-298	5%Co/ Base	250-260	1.0	0.075	0.3	3.7-9.9	7.4	291	250	1.0	0.075	0.3	3.8	15.7	2.2	8.2	21.5	23.5	28.9
299-310	2%Ni-5%Co/ Base	250-260	1.0	0.075	0.3	2.2-9.7	9.2	303	250	1.0	0.075	0.3	4.5	17.0	2.4	8.9	20.6	21.5	29.4
311-322	10%Co/ Base	250-260	1.0	0.075	0.3	3.9-20.2	12.9	.315	250	1.0	0.075	0.3	4.0	18.1	2.1	8.0	21.3	24.9	25.5
323-334	3%Co-6%Ni/ Base	250-260	1.0	0.075	0.3	3.7-10.4	12.2	327	250	1.0	0.075	0.3	4.0	16.4	3.4	8.5	21.0	23.2	27.5
358-367	2%Ni-5%Co/ MnO	250-300	1.0	0.199	0.2	2.6-9.0	6.9	361	250	1.0	0.20	0.20	2.8	27.7	5.0	8.3	21.4	19.5	18.1

Summary of FT + HZSM-5 Experiments (Follow-Bed Arrangement)

Run No (time-on-stream runs)	FT Catalyst	Ranges of Operating Conditions					Analysis of a Typical Run, wt %												
							Operating Conditions												
		Temp °C	Feed CO/H_2	Ft Cat.g	HZSM-5 g	Flow Rate mL/min	CO Conv. %	Typical Run No.	Temp °C	Feed CO/H_2	Ft Cat wt g	HZSM-5 g	Flow mL/min	C_1	C_2	C_3	C_4	C_5^+ (Aliphates)	Aromatics
172-176	3%Co + 6%Ni/ Base	250	1.0	0.1	0.1	15.0	6.3	175	250	1.0	0.1	0.1	15	18.3	7.0	11.6	23.7	32.6	6.8
177-186	10% Co/Base	250-275	1.0	0.1	0.1	9.4-16.1	9.8	182	250	1.0	0.1	0.1	9.4	13.0	2.7	10.5	24.2	41.3	8.4
187-193	"	260-275	1.0	0.1	0.15	8.5-16.0	7.0	190	260	1.0	0.1	0.15	8.9	20.3	2.7	8.7	19.3	27.7	21.2
194-205	"	260-275	1.0	0.1	0.15*	8.1	8.7	196	260	1.0	0.1	0.15	8.1	20.0	2.7	7.6	18.7	30.4	20.6
								197	260	0.5	0.1	0.15	8.1	29.7	3.6	6.8	16.1	27.7	16.3
206-216	"	250-275	1.0	0.1	0.302	3.9-8.9	13.7	209	250	1.0	0.1	0.30	8.3	12.8	2.4	9.4	20.0	34.9	20.5
							11.6	212	260	1.0	0.1	0.30	8.3	18.9	2.5	9.4	19.2	25.2	25.0
217-228	"	250-275	1.0	0.075	0.30	3.9-8.2	10.8	220	250	1.0	0.075	0.30	8.2	14.5	2.2	9.7	20.3	27.8	25.6
229-239	5% Co/ Base	250-260	1.0	0.075	0.3	3.7-9.0	2.6	233	250	1.0	0.075	0.3	9.0	16.4	2.6	9.2	22.8	25.8	23.3
240-244	5% Co/ Base	250-260	1.0	0.075	0	4.2-9.6	3.4	241	250	1.0	0.075	0.0	9.6	19.2	5.6	9.7	8.9	56.6	0.0
245-255	Base	250-260	1.0	0.075	0.3	3.4-8.4	13.3	247	250	1.0	0.075	0.3	9.7	17.2	9.9	9.9	15.8	15.5	31.8
256-264	25Ni-5%Co/Base	250-260	1.0	0.0753	0.3004	3.6-8.4	6.5	258	250	1.0	0.075	0.3	8.2	11.9	7.2	8.6	19.3	26.3	31.6
265-273	3%Co-6%Ni ase	250-260	1.0	0.0751	0.30	3.5-8.1	7.2	267	250	1.0	0.075	0.3	8.1	19.5	5.5	8.0	17.6	23.0	26.4
348-357	25Ni-5%Co/ MnO	250-300	1.0	0.2	0.2	3.1-9.8	3.8	348	250	1.0	0.2	0.2	9.3	27.4	5.4	9.7	22.8	11.7	17.1

*HZSM-5 calcined at 540°C

SECTION II

INTRODUCTION

This section covers the work done under the following Tasks:

Task F: Testing of FT-HZSM-5 combined catalyst in a 1/2 inch packed bed reactor.

Task G: Testing of FT-HZSM-5 and FT-ZMQ combined catalyst in a dual-bed microreactor.

EXPERIMENTAL

CATALYST PREPARATION FOR TASKS F&G:

A new batch of the co-precipitated base catalyst (5% Ni/ZrO_2) was prepared using the same procedure as described in Section I. The Ni/ZrO_2 catalyst (Base catalyst) thus prepared was used as a support for the preparation of 10% Co/base (FT) catalyst. The impregnation of this support with an aqueous cobaltous nitrate ($Co(NO_3)_2.6H_2O$) solution was carried out by the incipient wetness technique. The impregnated FT catalyst was dried in an oven at 100°C followed by calcination in a muffle furnace at 500°C for 24 h. The FT catalyst had the composition of 10% Co, 4.5% Ni and 85.5% ZrO_2. The BET surface area of the FT catalyst was 75 m^2/g.

A new batch of the HZSM-5 catalyst was also made according to the procedure given in the U.S. patent 4,112,056 (6). This procedure was different from the one used in earlier preparations of HZSM-5. The new procedure allowed the preparation of HZSM-5 using an ordinary pyrex flask thus eliminating the use of an autoclave which was required in the earlier preparations. The detailed procedure for making HZSM-5 is given in Appendix A. The BET surface area of this HZSM-5 catalyst was 370 m^2/g, which was in good agreement with the earlier value of 362 m^2/g (see Table 1, Section I).

The FT and HZSM-5 catalysts were pelletized and sieved to -12 + 24 mesh for activity tests. Catalyst "ZMQ" obtained from the "Centre de recherche industrielle du Quebec" was also crushed to the same particle size (-12+24 mesh) as FT and HZSM-5 catalysts. The FT catalyst was then physically blended with either HZSM-5 or catalyst ZMQ in the desired proportion. The FT catalyst was reduced <u>in-situ</u> with flowing hydrogen at 450°C for 16 hours. The catalyst temperature was lowered to the desired reaction temperature under flowing hydrogen before introducing the feed gas.

TASK F: Testing of FT-HZSM-5 combined catalyst in 1/2 inch packed bed reactor.

(i) Apparatus and procedure for 1/2 inch reactor experiments:

Synthesis gas conversion tests were carried out at atmospheric pressure in a down-flow 1/2 inch i.d. packed bed reactor as shown in Figure 1. The reactor was surrounded by a metal block heater whose temperature was controlled within $\pm 1^{\circ}C$ of the set temperature. The feed gas was preheated through a heated line prior to entering the reactor. At the end of each sequence of experiments, the liquid product from the condenser was collected and analyzed by gas chromatography. The uncondensed gas was continuously analyzed by on-line gas chromatographs. The details of the experimental programme for Task F are given in Table 1.

RESULTS AND DISCUSSION

(i) Testing of the FT-HZSM-5 Combined Catalyst in a 1/2 inch reactor

CO conversions and hydrocarbon product distribution with the time-on-stream using FT catalyst mixed with HZSM-5 are reported in Table 2 and plotted in Figure 2. As seen in Figure 2, a dramatic variation in the product distribution is observed during the first 10 h of operation. A sharp increase in the selectivities of C_5 fraction and aromatics with a simultaneous drop in the selectivities of (C_1+C_2) and (C_3+C_4) fractions is observed during this period. The Figure also shows that the selectivities of various fractions stabilize fairly well after about 10-12 h.

The effect of the operating variables on the selectivity is reported in Tables 3-5 and Figures 3-5.

Effect of flow rate (Table 3):

The effect of an increase in exit flow rate are as follows: (i) decrease in CO conversion (see Table 3) (ii) almost no variation in C_1, C_2, C_3, C_4 and C_5^+ selectivities. (See Figure 3)

Effect of H_2/CO ratio (Table 4):

Figure 4 clearly shows that an increase in H_2/CO ratio results in an increase in the methane content. Therefore, most of the experiments were carried out at H_2/CO ratio of 1. Figure 4 also shows that almost no variation in C_2 and C_3 selectivities, a slight drop in C_4 and C_5^+ selectivities.

Effect of temperature (Table 5):

Figure 5 clearly shows that C_1 and C_3 selectivities increase and C_5^+ fraction decreases with increase in temperature in the range of 225-300°C. It is well-known that high temperature operation of FT catalysts causes a shift in the product distribution towards low molecular weight compounds resulting in an increased methane content and a decrease in C_5^+ fraction (1,7).

Activity Behavior of Combined FT-HZSM-5 Catalysts

The activity tests were carried out with the 10% Co/base + HZSM-5 catalyst combination under fixed reaction conditions using the arrangement shown in Figure 6. The (hexane + liquid nitrogen) condenser shown in Figure 6 was used to condense the hydrocarbons. The temperature of this condenser was -94°C. These tests were carried out to fulfill the following objectives:

(i) To study the catalyst performance at higher conversion levels.

(ii) To make the overall material balance for the system operated for a long period of time.

(iii) To study the deactivation characteristics of the catalysts under the given operating conditions.

The operating conditions for these tests are listed in Table 6. The condensate samples from both the condensers (viz. the liquid nitrogen trap and ice condenser) for this series of experiments were sent for GC/MS analysis for the purpose analyses are given in Tables 7 and 8. The product analysis shows that most of the condensate is aromatic-containing mainly methyl and ethyl substituted benzenes and terminating at about A_{12} - A_{14}.

Since the conversion and product distribution varied during the test run (time-on-stream=199 h), the average values of all the runs were calculated in order to make an over-all material balance. The material balance is summarized in Figure 7. The hydrocarbon analysis of the total condensate (i.e. condensate from both the condensers) showed that over 78% of the hydrocarbons were heavier than C_{10}. The water content of the condensate has not been determined. Nevertheless, the hydrocarbon analysis suggests that the condensate largely consists of heavy hydrocarbons. If the condensate is assumed to contain 90% hydrocarbons, the overall material balance can be further presented as shown in Figure 8.

The variations of CO conversion and hydrocarbon distribution with time-on-stream for the above set of experiments are given in Figures 9-11. As shown in Figure 9 (curve b), the CO conversion declines with time-on-stream and the major decline take place during the initial stages of operation. As seen in Figure 10, a dramatic variation in the product distribution is observed during the first 24 h of operation. A sharp increase in selectivity of the C_5^+ fraction with a simultaneous drop in selectivity of the C_1-C_4 fraction is observed during this period. After 24 h, there is only a slight variation in the

product distribution. Figure 11 gives the fractions of ethylene in C_2 ($C_2^=/C_2$) and isobutane in C_4 ($i\text{-}C_4/C_4$) as a function of time-on-stream. The fraction of propylene in C_3 was very low (about 1.4%), and therefore, its variation with time-on-stream could not be determined precisely. The $C_2^=/C_2$ initially increases up to about 50 h and then decreases slightly. The $i\text{-}C_4/C_4$ ratio rapidly decreases initially but soon levels off to an average of 72%.

Activity Behavior of the FT Catalyst Alone.

The activity tests were carried out with the FT catalyst alone (10% Co/base) using the arrangement as shown in Figure 6 in order to draw important conclusions from the previously obtained results (i.e. 10% Co/base+HZSM-5 catalyst system). The operating conditions are reported in Table 9. The condensate sample collected from the condensers were weighed and analyzed by GC/MS for the purpose of product identification. The results of the product analysis are reported in Tables 10 and 11. It is seen that the products are essentially linear paraffins and olefins.

The variations of CO conversion and hydrocarbon distribution with time-on-stream for the above set of experiments using FT catalyst alone are plotted in Figure 9 and Figures 12 and 13. As shown in Figure 9 (curve a), the CO conversion declines with time-on-stream and the major decline takes place during the initial stages of the operation. Figure 12 shows that the selectivity to the C_3 and C_4 fractions slightly decreases, and that to C_1 increases with time-on-stream during the initial periods. The selectivity to C_2 and C_5^+ fractions exhibit almost no variation with time-on-stream. As shown in Figure 13, the fraction of olefin in both the C_2 as well as C_3 hydrocarbons initially increases with time-on-stream but later shows a declining trend giving a maximum at about 40-50 h of operation. At about the same time, the fraction of isobutane in C_4 fraction exhibits a broad minimum.

Variations in the Activity and Hydrocarbon product Distribution Produced by HZSM-5

The role of HZSM-5 in the modification of Fischer-Tropsch products can be delineated from the activity studies by comparing the product distributions obtained over FT catalyst with and without the presence of HZSM-5. It is seen from Figure 9 that the presence of HZSM-5 increases the CO conversion slightly but does not alter the trend of the conversion with time-on-stream. Increase in the conversion due to the presence of a zeolite component has also been reported in the literature (5).

A comparison of Figures 10 and 12 suggest the following important observations:

(i) During the initial stages, C_1 selectivity declines in the presence of zeolite (see Figure 10), while it increases in the absence of zeolite (see Figure 12). After about 24 h of operation, the methane selectivity is significantly lowered due to the presence of the zeolite. Such a decrease in the methane selectivity in the presence of HZSM-5 has also been reported (5).

(ii) Almost no variation in C_5^+ selectivity with time-on-stream is observed for FT synthesis alone. In contrast, for FT+HZSM-5 experiments, the C_5^+ selectivity is initially very low but dramatically increases within 24 h and later attains nearly the same level as obtained in the absence of the zeolite. This is attributed to the various cracking and aromatization reactions taking place over HZSM-5.

The changes in the compositions of lower hydrocarbons are observed by comparing Figures 11 and 13.

The presence of HZSM-5 results in significant reduction in olefinic content of the products. As a typical example, after about 24 h of operation, ethylene in C_2 fraction was 7% in the presence of zeolite, compared to 35% in its absence. Similarly, for C_3 fraction, the propylene percentage in the presence and absence of zeolite after 24 h of operation was 1.5% and 88% respectively. Thus it is seen that the reduction in the olefinicity of C_3 fraction is much higher compared to that of the C_2 fraction. A detailed comparison of C_4 fraction after about 24 h of operation is given in Table 12. Apart from the reduction of olefins, the percentage of isobutane increases significantly due to the presence of HZSM-5. These observations regarding the reduction of the olefins and increase in the formation of the isobutane in C_4 fraction are in accordance with the previously reported results (2-4). The changes are attributed to cracking and aromatization reactions which take place over HZSM-5.

(ii) Testing of the FT-ZMQ Combined Catalyst in a 1/2 inch Reactor

Catalyst ZMQ was used as a substitute for the HZSM-5 catalyst. The intent was to compare the results obtained under specified conditions using the catalyst ZMQ with those obtained with the HZSM-5 made in the laboratory.

The operating conditions for these tests are listed in Table 13. A typical overall product distribution obtained during this catalyst system is given in Table 14.

Comparison of Product Distribution using HZSM-5 and Catalyst ZMQ

The results obtained using catalysts HZSM-5 and ZMQ for a typical run (under the same conditions as shown in Table 3) are compared in Table 14 and are summarized as follows:

(i) It is seen that the catalyst ZMQ makes less aromatics as compared to HZSM-5.

(ii) Using catalyst ZMQ the products are more olefinic in nature and contain lower percentages of isobutane in C_4 fraction.

(iii) In the presence of zeolite HZSM-5, the olefins formed by the FT catalyst are converted into aromatics with simultaneous formation of isobutane. Low yields of aromatics and isobutane with corresponding higher olefinicity of the product obtained using catalyst ZMQ indicate that the aromatization selectivity of catalyst ZMQ is not as high as that of the ZSM-5 under these operating conditions.

It is possible that pressure may improve the yield of aromatics and C_5^+ hydrocarbons at high pressures.

With the above set of experiments, Task F has been completed.

TASK G: Testing of FT-HZSM-5 and ZMQ Combined Catalyst in a Dual-Bed Microreactor

(I) Apparatus and Procedure for Dual-Bed Microreactor Experiments

In a single stage process, the zeolite is physically admixed with a CO reduction catalyst such as FT catalyst or methanol synthesis catalyst (3-5). Since a single stage process does not permit the operation of each component at its optimum reaction conditions, it is highly desirable to separate the two beds so that each catalyst bed can be operated at its optimum condition.

In the two-stage process, the products from FT reactor are fed to another reactor containing zeolite HZSM-5 (8).

The main advantages of the two-step process (dual-bed set-up) are as follows:

(i) The dual-bed reactor system offers considerable flexibility in controlling the operating conditions and, thus, the product distribution.

(ii) The dual-bed reactor system allows the operation of each component at its optimum reaction conditions.

(iii) The dual-bed reactor system permits easier regeneration and replacement of the spent catalyst. The FT catalyst usually deactivates faster than the HZSM-5 catalyst. Therefore, FT catalyst may require regeneration or replacement while HZSM-5 catalyst is still active.

In view of the above advantages, we have studied the synthesis of hydrocarbons in a dual-bed microreactor system.

The apparatus consisted of two reactors connected in series with separate temperature control arrangements as shown in Figure 14. The first reactor (used as the FT reactor) was the same 1/4" OD reactor-preheater assembly as used in the earlier microreactor experiments. The second reactor (containing HZSM-5) was made of 1/4" OD stainless steel tube and was surrounded by an aluminum block heater. The 1/4" OD line connecting the two reactors was kept heated to prevent condensation of the products. The synthesis gas was passed through the first reactor containing 10% Co/Zr base catalyst and the resulting product mixture then was fed to the second reactor containing HZSM-5 or catalyst ZMQ. The products from the second reactor were analyzed by on-line gas chromatographs. In all the experiments, the temperature of the FT catalyst bed was fixed at 250^{o}C while the temperature of the HZSM-5 bed was varied from 250^{o}C to 400^{o}C. The summary of the experimental runs is given in Table 15.

RESULTS AND DISCUSSION

(i) Testing of the FT-HZSM-5 Catalyst in a Dual-Bed Microreactor.

Various HZSM-5/FT ratios (see Table 15) were used and the HZSM-5 reactor temperature varied from 250-400°C. Fig. 15 compares typical chromatograms obtained when the temperature of HZSM-5 reactor (HZSM-5/FT ratio = 2) was raised from 250°C in increments of 50° and held at the increased temperature for about 1 h before the product sample was taken for analysis. The formation of higher aromatics (A_{10}) follows a rather interesting trend. As the temperature of the HZSM-5 reactor is raised from 250° to 300°C, higher aromatics are observed in the product stream, of which A_{12} is prominent (see Figs. 15 (a-1) and (a-2)). At 350°C, A_{13} is formed while A_{12} now decreases (Fig. 15 (a-3)). As the temperature is raised further to 400°C, the peaks for A_{12} and A_{13} shrink, but the peak for A_{14} becomes prominent. Fig.15(a-5) shows the effect when a temperature of 400°C is maintained for a longer time; the peaks for all the higher aromatics become very small in size.

As the temperature of HZSM-5 reactor is raised, the peak for A_6 becomes more prominent and remains prominent even if the higher temperature is maintained for a long period.

Fig. 15 (b) shows the chromatograms obtained over Chromosorb 102 column which shows the distribution of lower hydrocarbons in greater detail. It is interesting to observe that as the temperature is increased, the size of ethylene peak increases remarkably.

Table 16 gives the product analyses obtained on the basis of chromatograms shown in Figure 15. The Table shows clearly that the C_2 fraction increases and the C_5^+ fraction decreases as the temperature of the HZSM-5 reactor is increased.

Table 17 gives the steady-state product distributions versus reactor temperature for HZSM-5/FT ratio of 1 and are plotted in Figures 16-19. Figure 17 shows that the selectivities of C_1, C_2 and C_3 fractions increase, while that of C_4 and C_5^+ fractions decrease as the temperature of HZSM-5 reactor is increased. Figure 16 indicates that the selectivity of C_5^+ aliphatics decreases while that of total aromatics passes through a maximum with an increase in temperature of the HZSM-5 reactor. Figure 19 shows that with an increase in the temperature of the HZSM-5 reactor, the ethylene selectivity in C_2 fraction increases; on the other hand, the propylene selectivity in the C_3 fraction exhibits a minimum, while the isobutane selectivity in C_4 fraction exhibits a maximum with increase in temperature (Figure 18). The temperature (in the range 275-300°C) which corresponds to a maximum in the aromatic selectivity (Figure 16) also corresponds approximately to a minimum for C_3 fraction (Figure 19) and a maximum for the isobutane fraction (Figure 18). Approximately similar trends are observed for similar experiments with HZSM-5/FT ratio of 2 and 4 although the magnitude of various fractions differs due to the increased amount of HZSM-5. The results for HZSM-5/FT ratio of 2 and 4 are reported in Tables 16 and 18 and are plotted in Figures 20-27.

Summary of the Effect of HZSM-5/FT Ratio on Product Distribution in the Dual Bed Microreactor

(1) Effect of HZSM-5/FT Ratio on Selectivity

From Figures 16-27 it is seen that increasing the HZSM-5/FT ratio while keeping both the reactors at 250°C resulted in:

(i) a decrease in the selectivity of the C_5^+ (aliphatics) fraction with a corresponding increase in the aromatics production. A decrease in C_5^+ aliphatics with an increase in the HZSM-5/FT ratio suggests that the zeolite component alters the selectivity by converting these fractions into aromatics through cracking/oligomerization reactions.

(ii) an increase in the selectivity of the isobutane

(iii) a decrease in the olefinicity of the C_2 and C_3 fractions. These results suggest that at lower HZSM-5/FT ratios, the time of contact with HZSM-5 is not sufficient for the conversion of all the olefins and other hydrocarbons which are produced by the FT catalyst.

(2) Effect of HZSM-5/FT Ratio on Aromatic Production

The effect of HZSM-5/FT ratio versus total aromatics is plotted in Figure 28. It is seen from Figure 28 that increasing the HZSM-5/FT ratio results in an increase in the aromatics production while maintaining the HZSM-5 reactor in the temperaure range 250-300°C. For temperatures above 300°C, increasing the HZSM-5/FT ratio from 2 to 4 results in a tremendous decrease in the amount of aromatic production. This is an extremely important result and has not been reported in the literature. Therefore, the production of aromatics was found to be maximized for an HZSM-5/FT ratio of 4 and at a HZSM-5 reactor temperature of 300°C. At these conditions, the aromatic production was found to represent 45.5 wt% (see Figure 28) of the total hydrocarbons produced.

For the microreactor follow-bed experiments (Section I) the maxiumum amount of aromatics produced was 30 - 35 wt % at the optimum operating

conditions (1 atm, 250-280°C). Now, in dual-bed microreactor experiments, the independent control of the temperature of the FT and HZSM-5 catalyst increases the aromatic production to 45.5%. This again illustrates that the production of aromatics is very sensitive to the operating conditions being used.

(ii) Testing of the FT-ZMQ Combined Catalyst in a Dual Bed Microreactor

Testing of the catalyst ZMQ was conducted using the dual bed microreactor. The experiments conducted were intended to determine whether catalyst ZMQ behaves in a manner similar to that of HZSM-5 under the same operating conditions, except that the flow rate was different. The effect of changing the flow rate does not have any effect on the selectivities except the CO conversion (see Table 3).

The effect of varying the temperature of the catalyst ZMQ bed between 250 and 400°C on the product distribution is shown in Table 19. The results are also plotted in Figures 29-32 for Catalyst ZMQ/FT ratio of 4. Increasing the temperature of the catalyst ZMQ bed results in the following observations:

(i) a slight initial increase in the production of the (C_1 + C_2) fraction as the temperature is increased from 250 to 275°C. After about 300°C, the (C_1 + C_2) fraction remains constant with increasing temperature (Figure 30).

(ii) an increase in the selectivity of C_3 fraction (Figure 30).

(iii) a slight maximum is observed for the C_4 fraction (Figure 30).

(iv) a pronounced decrease in the selectivity of C_5^+ aliphatics (Figure 29).

(v) a slight initial decrease in the production of aromatics as the temperature is increased from 250 to 300°C. After 300°C, the aromatics make remains constant (Figure 29).

(vi) a substantial increase in the olefinicity of the C_2 and C_3 fractions (Figure 31).

(vii) a decrease in the amount of i-C_4 in the C_4 fraction (Figure 32).

Similar trends are observed for similar experiments with catalyst ZMQ/FT ratio of 1. The results for catalyst ZMQ/FT ratio of 1 are shown in Table 20 and are plotted in Figures 33-36.

Summary of the Effect of Catalyst ZMQ/FT Ratio on Product Distribution in the Dual Bed Microreactor

Increasing the catalyst ZMQ/FT ratio from 1 to 4 while keeping both the reactors at 250°C resulted in (see Table 21):

(i) almost no variation in the selectivity of C_1-C_5 fractions.

(ii) a decrease in the olefinicity of C_2 and C_3 fractions.

(iii) an increase in the selectivity of the isobutane.

(iv) a slight increase in aromatic production.

The results suggest that at lower catalyst ZMQ/FT ratios, the time of contact with catalyst ZMQ is not sufficient for the conversion of all the olefins and other

hydrocarbons which are produced by the FT catalyst. This behavior is similar to that observed when the HZSM-5/FT ratio was increased.

Comparison of Produt Distribution Using HZSM-5 and Catalyst ZMQ

Although catalyst ZMQ was found to have similar effects on the product distribution as HZSM-5, there still existed some important differences. These differences are reported in Table 22, and are summarized as follows:

(i) the HZSM-5 was found to produce greater amounts of aromatics as compared to that produced when using catalyst ZMQ.

(ii) catalyst ZMQ produces substantially larger amounts of C_5^+ aliphatics than HZSM-5.

(iii) the olefinicity of the product stream is much greater when using catalyst ZMQ as compared to that obtained when using HZSM-5. The $C_3^=$ fraction is much larger while the i-C_4 fraction is much lower when using catalyst ZMQ as compared to that produced when using HZSM-5.

Thus, the low yields of aromatics and isobutane with corresponding higher olefinicity of the product obtained using catalyst ZMQ indicate that the aromatization selectivity of catalyst ZMQ is not as high as that of the HZSM-5.

With the above set of experiments, Task G has been completed.

SUMMARY AND CONCLUSIONS

TASK F

The role of the HZSM-5 catalyst for the modification of Fischer-Tropsch reaction products was delineated by comparing the product distributions obtained over FT catalyst with and without the presence of HZSM-5. The major conclusions are as follows:

(i) The presence of HZSM-5 catalyst increases the CO conversion slightly.

(ii) C_1 selectivity declines in the presence of the zeolite while it increases in the absence of the zeolite.

(iii) The presence of HZSM-5 results in significant reduction in olefinic content of the products. Apart from reduction in olefins, the percentage of isobutane increases significantly due to the presence of HZSM-5.

Comparison of catalyst ZMQ with HZSM-5 catalyst from the 1/2 inch reactor experiments suggests the following conclusions:

(i) The catalyst ZMQ makes less aromatics compared to HZSM-5.

(ii) Using catalyst ZMQ, the products are more olefinic in nature and contain lower percentage of isobutane in C_4 fraction. The low yields of aromatics and isobutane with corresponding higher olefinicity of the products suggests that the aromatization activity of the catalyst ZMQ is not as high as that of HZSM-5. However, it may change for the better at high pressures.

TASK G

In the dual bed microreactor system, increasing the HZSM-5/FT ratio while keeping both the reactors at 250°C resulted in:

(i) a decrease in the selectivity of the C_5^+ (aliphatics) fraction with a corresponding increase in the aromatics production.

(ii) an increase in the selectivity of isobutane.

(iii) a decrease in the olefinicity of the C_2 and C_3 fractions.

Increasing the HZSM-5/FT ratio also resulted in an increase in the aromatics production while maintaining the HZSM-5 reactor in the temperature range 250-300°C. The production of the aromatics was maximized at a HZSM-5/FT ratio of 4 and HZSM-5 reactor temperature of 300°C. At these conditions, the aromatic production was 45.5 wt% of the total hydrocarbons.

Increasing the catalyst ZMQ/FT ratio while keeping both the reactors at 250°C resulted in :

(i) an increase in the selectivity of isobutane.

(ii) a decrease in the olefinicity of C_2 and C_3 fractions.

(iii) a slight increase in the aromatics production. Although catalyst ZMQ was found to have similar effect on the product distribution as HZSM-5, there

still were some important differences. These are as follows:

(i) The catalyst HZSM-5 was found to produce greater amounts of aromatics than the catalyst ZMQ.

(ii) Catalyst ZMQ produces substantially larger amounts of C_5^+ aliphatics than HZSM-5.

(iii) The C_3 fraction is much larger while the i-C_4 fraction is much lower when using catalyst ZMQ as compared to that when HZSM-5 is used.

Thus, the low yields of aromatics and isobutane with corresponding higher olefinicity of the product obtained using catalyst ZMQ indicate that the aromatization activity of catalyst ZMQ is not as high as that of the HZSM-5. At this point we do not understand this behavior. More work needs to be done to clarify this situation. It is possible that pressure may improve the catalyst ZMQ operation i.e. it may yield more aromatics + C_5^+ aliphatics at high pressures.

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APPENDIX - A

Reference: Preparation of Zeolites by Chen et al., U.S. Pat. 4,112,056 (1973)

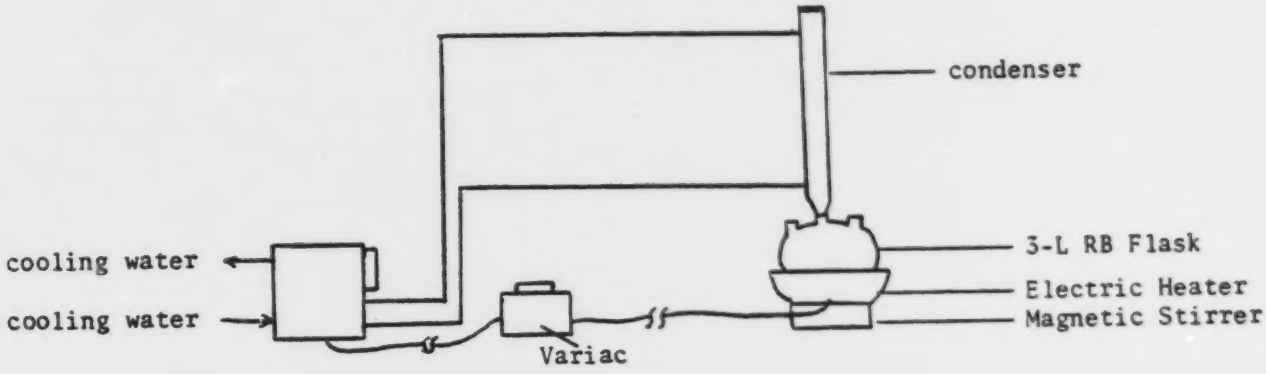
Preparation of HZSM-5

A/ MATERIALS REQUIRED:

(i) Sodium Aluminate
(ii) Sodium Hydroxide Pellets
(iii) Sodium Silicate Solution, Tech. (Fischer Scientific)
(iv) Tetrapropylammonium Bromide (Aldrich)
(v) Sulfuric Acid (98%)
(vi) Sodium Cholride
(vii) Hydrochloric Acid

B/ EQUIPMENT REQUIRED:

(i) 3-L Round Bottom Flask
(ii) Condenser
(iii) Magnetic Stirrer
(iv) Electric Heater
(v) Waring Blender
(vi) 4-L Beaker
(vii) 18 cm dia. Buckner Funnel
(viii) 2-L Filtering Flask
(ix) Waterman Filtering Paper
(x) Variac



C/ EXPERIMENTAL PROCEDURE:

(1) The initial step in producing HZSM-5 is the preparation of the following solutions:

Solution A: -2.5 gm Sodium Aluminate
-0.17 gm Sodium Hydroxide
-66.0 gm Distilled water

Solution B: -211.2 gms Sodium Silicate
-2.64 gms Distilled water

Solution C: -26.4 gms Tetrapropylammonium Bromide
-132.0 gms Distilled water

Solution D: -21.0 gms Sulfuric Acid
-66.0 gms Distilled water

Solution E: -79.2 gms Sodium Chloride
-95.0 gms Distilled water

(2) Solutions B,C,D, and E are combined and mixed in a waring blender for approxiamtely 10 minutes.

(3) The mixture is then placed in a 3-L pound bottom flask and was heated to 100°C with a magnetic stirring providing agitation.

(4) 10% of solution A is added initially.

(5) The resulting mixture is maintained at a temperature of 100°C and refluxed for a 240 h period.

(6) Solution A is added to the heated mixture in the following sequence:

-10% of solutions A for the first 3 days
-57% of remaining solution A is added for each succeeding day after 3 days.

(7) After refluxing for 10 days the mixture is cooled to room temperature and then filtered through fast qualitative filter paper under vaccuum.

(8) The crystals are then washed 3 times with hot distilled water and then dried at 110°C.

(9) The crystals are then put in a muffle furnace at 550°C for 16 h to remove organic molecules.

(10) The crystals are then refluxed for 24 h in 2.0 L of 0.5 M HCl to ion exchange impurities in the crystal and to set sodium in crystal.

(11) The crystals are then filtered and washed as before (steps 7-8).

(12) The crystals are then dried in air at 110°C and finally in a muffle furnace at 400°C for 4 h

Table 1. Summary of experimental runs for Task F: Testing of FT-HZSM-5 combined catalyst in 1/2" packed bed reactor.

Run No.	Catalyst	Operating Conditions		
		HZSM-5/FT Ratio (or) ZMQ	Temperature, °C	H_2/CO
422-455	10% Co/Zr Base (1.0 g) + HZSM-5 /FT (4.0 g)	4	255-300	1,2,3
456-498	10% Co/Zr Base (4.0 g) + HZSM-5 (12.0 g)	3	250	1
499-533	10% Co/Zr Base alone	0	250	1
534-558	10% Co/Zr Base (4.0 g) + catalyst ZMQ (12.0 g)	3	250,300	1

Table 2. Product Distribution wit Time-on-stream*

Run No.	Operating Conditions			Product Distribution					
	Time on stream h	Exit Flow rate, mL/min	Temp °C	CO Conv. %	C_1	C_2	C_3	C_4	C_5+	Aromatics A_6-A_9
422	1	9.8	250	36.3	23.7	2.8	11.9	44.6	17.0	1.9
423	2	10.6	252	34.4	21.4	2.5	12.2	39.8	24.1	4.9
424	3	10.9	252	31.6	18.6	2.0	12.1	36.2	31.1	8.9
425	4	5.2	251	33.8	16.6	1.6	12.7	32.6	36.5	14.2
426	22	11.4	253	19.2	15.1	1.0	10.8	24.5	48.6	22.9
427	25.2	20.6	252	13.1	15.2	1.2	10.0	24.2	49.2	21.2
428	26.7	50.0	250	6.4	13.2	1.5	8.3	21.8	55.2	21.5
429	28	95.2	253	4.9	14.2	2.2	9.1	23.8	50.7	18.1

*CO hydrogenation using 1/2" reactor
FT catalyst: 10% Co/zirconia base
Bed arrangement: mixed
Wt. of FT Catalyst: 1.0 g
Wt. of HZSM-5: 4.0 g
Particle size range of each component: -12+24 mesh
Feed: 39.9% CO, 20.0 Ar, 40.1 H_2
C_5+ includes aromatics

Table 3. Effect of flow rate on product distribution*

Run No.	Exit flow rate, mL/min	Conv. %	Product Distribution, wt%					
			C_1	C_2	C_3	C_4	C_5^+	Aromatics A_6-A_9
444	3.4	5.9	20.1	2.1	9.8	24.5	43.5	19.3
445	5.1	3.9	18.7	2.6	9.0	22.6	47.1	21.6
446	6.5	2.7	20.2	3.8	9.6	22.6	43.8	14.0
447	7.9	2.0	20.4	4.5	10.3	23.0	41.8	14.6

*CO hydrogention using 1/2" reactor
FT catalyst: 10% Co/Zirconia base
Bed arrangement: mixed
Wt. of FT catlayst: 1.0 g
Wt. of HZSM-5 Catalyst: 4.0 g
Particle size range of each component: -12+24 mesh
Feed: 39.9% CO, 20.0% Ar, 40.1% H_2
Reaction temperature: 250°-254°C
C_5^+ includes aromatics

Table 4: Effect of feed composition on product distribution*

Run No.	H_2/CO ratio	Conv. %	Product Distribution, wt%					
			C_1	C_2	C_3	C_4	C_5^+	Aromatics A_6-A_9
450	1	10.9	24.4	1.7	11.7	26.8	35.4	15.0
448	2	14.0	34.3	2.99	10.4	24.7	27.7	7.5
449	3	18.9	39.6	3.6	8.5	18.9	29.4	11.9

* Reaction temperature 250-252°C
Exit flow rate - 14-21 mL/min
C_5^+ fraction includes aromatics

Table 5: Effect of reaction temperature on product distribution*

Run No.	Temp.	Conv. %	Product Distribution, wt%					
			C_1	C_2	C_{3-}	C_4	C_5+	Aromatics** A_6-A_9
451	225	3.3	17.2	2.0	10.4	25.5	44.9	-
452	250	16.4	31.9	2.5	15.5	28.8	21.3	-
453	275	15.7	33.9	2.4	14.2	25.4	24.1	-
455	300	28.9	39.0	2.8	19.7	19.7	18.8	-

* Exit flow rate: 13-15 mL/min
Feed Composition = 39.9% CO, 20.0% Ar, 40.1% H_2
C_5+ fraction includes aromatics

**Total aromatics content was inconsistent for reasons unknown. (It was fluctuating between high and low)

Table 6: Operating Conditions for Runs 456 to 498.

FT Catalyst: 10% Co/Zirconia base
Wt. of FT catalyst: 4.00 g
Wt. of HZSM-5: 11.8245 g
Particle size range of both catalysts: -12+24 mesh (Tyler Equiv.)
(0.0555" - 0.0278").

Feed composition: 40% CO, 40% H_2, 20% Ar (by vol.)
Avg. Reactor Temperature: 250°C
Feed Flow Rate: 21.4 mL/min
Catalyst Pretreatment: Reduced at 450°C under H_2 for one day, cooled at 250°C under flowing H_2 and maintained under H_2 at 250°C for 4 days.
Reactor Size: 1/2" i.d.
Bed Arrangement: Mixed Bed
Total time of operation (#456 to 498): 199 h
Average CO conversion: 33.6 mol% (as determined from TCD)

Table 7. Results of GC/MS Analysis for Runs 456 to 498*
(Condensate from Liquid Nitrogen Trap)

A. Top Layer

Carbon No.	Major Components	Approximate Area %
C_9	1-ethyl-2methyl-cyclohexane (trans and cis)	0.5
A_8	Ethyl benzene 1,3 dimethyl benzene 1,2 dimethyl benzene 1,4 dimethyl benzene	80.2
A_9	1,2,4 trimethyl benzene 1,2,3 trimethyl benzene 1-ethyl 2-methyl benzene 1-methyl ethyl benzene	19.0
A_{10}	1-ethyl 2,4-dimethyl benzene 1,1 dimethyl ethyl benzene	0.3
		100.0

* NOTE: The condensate was mixed with chloroform in an effort to dissolve the hydrocarbons, however, the mixture resulted in two layers. The analysis of both top and bottom layers are given.

Table 7. Con't

B. Bottom Layer ($CHCl_3$ Layer)

Carbon No.	Major Components	Approximate Area %
A_8	1,2 dimethyl benzene) 1,3 dimethyl benzene) 1,4 dimethyl benzene) ethyl benzene	76.9
A_9	1-methyl ethyl benzene) 1-ethyl-2-methyl benzene) 1-ethyl-3-methyl benzene) 1,2,4-trimethyl benzene) 1,2,3-trimethyl benzene) 1,3,5-tri methyl benzene)	22.0
A_{10}	2-ethyl 1,4-dimethyl benzene) 4-ethyl 1,2-dimethyl benzene) 2-ethyl 1,3-dimethyl benzene) 1,2,3,4-tetramethyl benzene) napthalene	0.8
A_{11}	1-methyl naphthalene) 2-methyl naphthalene)	0.3
		100.0

Table 8. Results of GC/MS Analysis for Runs 456-498 (Condensate from Ice Condenser) (Mixed with Chloroform)

A. Top Layer

Carbon No.	Major Components	Approximate Area %
A_7	methyl benzene	4.9
A_8	1,2 dimethyl benzene) 1,4 dimethyl benzene) ethyl benzene)	15.6
A_9	1-methyl ethyl benzene) 1-ethyl 2-methyl benzene) 1-ethyl 4-methyl benzene)	10.8
A_{10}	naphthalene) 1,1 dimethyl 2-propenyl benzene)	5.1
A_{11}	2-methyl naphthalene) 1-methyl naphthalene)	25.5
A_{12}	2-ethyl naphthalene) 1-ethyl naphthalene) 1,2-dimethyl naphthalene) 1,3-dimethyl naphthalene) 2,3-dimethyl naphthalene) 1,5-dimethyl naphthalene) 1,4-dimethyl naphthalene)	34.4
A_{13}	2-(1-methyl ethyl naphthalene) 1-(1-methyl ethyl naphthalene) 1,3,6-trimethyl naphthalene)	3.7
		100.0

Table 8. Con't

B. Bottom Layer ($CHCl_3$) Layer

Carbon No.	Major Components	Approximate Area %
A_8	ethyl benzene) 1,2 dimethyl benzene) 1,4 dimethyl benzene)	14.3
A_9	propyl benzene) 1-ethyl 2-methyl benzene) 1-ethyl 4-methyl benzene) 1-methyl ethyl benzene) 1,2,3-trimethyl benzene) 1,2,4-trimethyl benzene) 1,3,5-trimethyl benzene)	12.8
A_{10}	1-ethyl 2,3 dimethyl benzene) 2-ethyl 1,3 dimethyl benzene) 2-ethyl 1,4 dimethyl benzene) 4-ethyl 1,2 dimethyl benzene) 1,2,3,5 tetramethyl benzene) 1,2,3,4 tetramethyl benzene) naphthalene	8.7
A_{11}	1,1-dimethyl 2-propenyl benzene) 2-methyl naphthalene) 1-methyl naphthalene)	25.0
A_{12}	1-ethyl naphthalene) 2-ethyl naphthalene) 1,2-dimethyl naphthalene) 1,7-dimethyl naphthalene) 1,8-dimethyl naphthalene) 1,4-dimethyl naphthalene) 2,6-dimethyl naphthalene)	31.1
A_{13}	2-(1-methyl ethyl) naphthalene) 1-methyl ethyl naphthalene) 2,3,6-trimethyl naphthalene) 1,6,7-trimethyl naphthalene)	8.0
A_{14}	1-methyl-7-(1-methyl ethyl) naphthalene 1-(1,1-dimethyl ethyl) naphthalene	0.1
		100.0

Table 9. Operating Conditions for Runs 499-533

FT Catalyst	10% Co/Zirconia base
Amt. of Catalyst	4.0 g
Particle size range	-12+24 mesh
Feed composition	40% CO, 40% H_2, 20%Ar (by volume)
Reactor Temperature	250°C
Feed inlet flow rate	20.5 mL/min
Catalyst Pretreatment	reduced under H_2 at 450°C for one day
Reactor size	1/2" i.d.
Bed arrangement	FT catalyst only
Total time of oepration (#499-533)	128.5 h

TABLE 10 Results of GC/MS Analysis for Runs 499-533: Condensate from Liquid Nitrogen Trap

A. Top Layer - wt. of condensate = 0.4497 g

Carbon No.	Major Compounds	Approximate Area %
C_6	2 - methyl - 1 - pentanol 2 - ethyl - 1 - butanol	1.6
C_7	heptane 3 - heptene 2 - heptene 3 - methyl - 2 - hexene 4 - methyl - 2 - hexene 3 - ethyl - 1 - pentene	11.3
A_7	methyl benzene	2.7
C_8	3 - methyl heptane 3,4 - dimethyl hexane 4,5 - dimethyl - 1- hexene 2,4 - dimethyl hexane 1,1,2 - trimethyl cyclopentane 1,2,3 - trimethyl cyclopentane pentyl cyclopropane octane isooctanol	36.3
A_8	Ethyl benzene 1,2 - dimethyl benzene 1,4 - dimethyl benzene	2.7
C_9	4 - methyl octane 2,3,4 - trimethyl hexane 2,4 - dimethyl heptane 3 - methyl octane 3,3 - dimethyl heptane 1,2,3 - trimethyl cyclohexane 1 - methyl - 2 - pentyl cyclopropane 4 - ethyl - 3 - heptane nonane 1 - nonanol 1 - methyl - 2 - propyl cyclopentane	32.9

TABLE 10 Con't

Carbon No.	Major Compounds	Approximate Area %
C_{10}	4 - methyl nonane 2,5 - dimethyl octane 2,6 - dimethyl octane 5 - decene 4 - decene 2 - methyl - 4 - nonene decane	11.2
C_{11}	undecane 2,4,6 - trimethyl octane 4,5 - dimethyl nonane	1.2
		100.0

B. **Bottom Layer - wt. of condensate = 0.2708 g**

Carbon No.	Major Compounds	Approximate Area %
C_9	nonane 4 - ethyl - 2 - methyl hexane	30.2
C_{10}	5 - decene 4 - decene 2 - methyl - 4 - nonene decane	13.6
C_{11}	undecane 2,4,6 - trimethyl octane	33.8
C_{13}	2,5,6 - trimethyl decane 4,6 - dimethyl undecaen 4,7 - dimethyl undecane	22.3
		100.0

TABLE 11 Results of GC/MS Analysis for Runs 499-533: Condensate from Ice Condenser

A. Top Layer - wt. of condensate = 0.7503 g

Carbon No.	Major Compounds	Approximate Area %
C_8	octane 3 - ethyl hexane	1.2
C_9	nonane 4 - ethyl - 2 - methyl - hexane 2,3,4 - trimethyl hexane 4 - methyl octane 3 - methyl octane 3,5 - dimethyl heptane 1 - methyl - 2 - pentyl cyclopropane 1 - nonanol 4 - ethyl - 3 - heptene 1 - methyl - 2 - propyl cyclopentane 4 - ethyl - 2 - methyl hexane	9.0
C_{10}	1,2 - dimethyl 2 - pentyl cyclopropane 1,2 - dimethyl 3 - pentyl cyclopropane 5 - methyl nonane 2,3,3 - trimethyl hexane 4 - methyl nonane 2,5 - dimethyl octane 2,3 - dimethyl octane 2 - methyl nonane 3,5,5 - trimethyl - 1 hexene	15.3
C_{11}	5 - methyl decane 2,5 - dimethyl nonane 2,3 - dimethyl nonane 2 - methyl decane 3 - methyl decane 2 - undecene 4 - undecene 5 - undecene 3 - undecene 1 - undecene 2 - methyl - 3 - decene undecane 6 - ethyl - 2 - methyl octane	20.4

TABLE 11 Con't

Carbon No.	Major Compounds	Approximate Area %
C_{12}	5 - methyl undecane 3,4 - dimethyl decane 5,6 - dimethyl decane 4 - methyl undecane 3 - methyl undecaen 1 - dodecene 1 - dodecanol 5 - methyl - 4 - undecene 2 - methyl - 2 - undecene	16.9
C_{13}	6 - methyl dodecane 2,5 - dimethyl undecane 2,6 - dimethyl undecane 2,3 - dimethyl undecane 4 - methyl dodecane 2,3,4 - trimethyl decane 6 - tridecene 1 - tridecene tridecane 4,4 - dimethyl undecane 3 - ethyl undecane	10.1
C_{14}	6 - methyl tridecane 5 - methyl tridecane 4 - methyl tridecane tetradecane	2.9
C_{15}	2 - methyl tetra-decane 2,5 - dimethyl tridecane pentadecane	8.9
C_{16}	hexadecane	8.3
C_{17}	heptadecane	7.0
		100.0

TABLE 11 Con't

B. Bottom Layer - Wt. of condensate - 4.6621 g

Carbon No.	Major Compounds	Approximate Area %
C_9	4 - ethyl heptane nonane 4 - ethyl - 2 - methyl hexane 3,4 - dimethyl heptane 1 - nonanol	3.1
C_{10}	4 - methyl nonane 2,5 - dimethyl octane 2,3 - dimethyl octane 3 - methyl nonane 2,6 - dimethyl octane 2 - propyl heptane 4 - propyl - 3 - heptane 2 - methyl - 4 - nonene 4 - ethyl - 3 - octene 2,6 - dimethyl - 3 - octene 1 - decene 1 - decanol 5 - decene 4 - decene decane	13.7
C_{11}	2,6,6 - trimethyl octane 2,3,7 - trimethyl octane 2,4,6 - trimethyl octane 5 - methyl decane 2,5 - dimethyl nonane 4 - methyl decane 2,3 - dimethyl nonane 3 - methyl decane 4 - undecene 5 - undecene undecane	19.2
C_{12}	3 - methyl undecane 1 - dodecanol cyclododecane 2 - methyl - 2 - undecene 1 - butyl - 2 - propyl cyclopentane 3,6 - dimethyl decane 1 - dodecene	16.0

TABLE 11 Con't
Bottom Layer

Carbon No.	Major Compounds	Approximate Area %
C_{13}	4,7 - dimethyl undecane 2,3 - dimethyl undecane 6 - methyl dodecane 2,5 - dimethyl undecane 2,6 - dimethyl undecane 5 -(1 - methyl propyl)-nonane 4 - methyl dodecane 2,3,4 - trimethyl decane 3 - methyl dodecane 3,9 - dimethyl undecane 2,9 - dimethyl undecane	16.3
	6 - tridecene 1 - tridecene 2 - methyl - 2 - dodecene tridecene 4,4 - dimethyl undecane 3 - ethyl undecane 2,10 - dimethyl undecane 2 - methyl - 5 - propyl nonane	
C_{14}	1 - tetradecanol 6 - methyl tridecane 2,5 - dimethyl dodecane 5 - methyl tridecane 4 - methyl tridecane tetradecane 6 - methyl tridecane	12.7
C_{15}	2 - methyl tetradecane 2,5 - dimethyl tridecane pentadecane	7.9
C_{16}	hexadecane	7.1
C_{17}	heptadecane	2.8
C_{18}	octadecane	1.0
		100.0

Table 12. Comparison of C_4 Hydrocarbons*

	FT Catalysts Only	FT + HZSM-5
C_4 Selectivity**	8.4	22.5
C_4 Distribution, percent:		
isobutane	0.8	68.9
n-butane	15.2	26.3
1-butene	42.0	
iso-butylene	5.9	4.8
cis-2-butene	15.3	
trans-2-butene	20.8	

* time-on-stream -- approx. 24h, other operating conditions listed in Tables 6 and 9.

** Wt. % of total hydrocarbons

Table 13. Operating Conditions for Runs 534-558

FT Catalyst: 10% Co/Zirconia base

Particle size of FT catalyst: -12+24 mesh

Wt. of FT catalyst: 4.0 g

Wt. of ZMQ: 12.0 g

Feed composition: 40% CO, 40% H_2, 20% Ar

Total feed rate: 21 mL/min

Reactor Temperature: 250°C (For Runs 534 to 557)
300°C (For Runs 558)

Bed Arrangement: Mixed Bed

Total Time of Operation (#534 to 558): 76 h

Table 14. Comparison of Product Distribution

Run No.	547	461
Catalyst	FT + Cat. ZMQ	FT + HZSM-5
Time-on-stream, h	26	26
CO Conversion, %	30.3	33.0
H.C. Distribution (wt%)		
C_1	20.9	15.1
C_2	3.4	1.0
C_3	6.5	13.2
C_4	19.9	22.3
C_5+ (including aromatics)	49.3	48.4
Total Aromatics, wt%	11.8	30.5
C_2=/Total C_2, %	28	7.4
C_3=/Total C_3, %	55	1.4
i-C_4/Total C_4, %	33	72.0

Table 15. Summary of Experimental Runs for Task G: Testing of FT-HZSM-5 and FT-ZMQ Combined Catalyst in a Dual-Bed Microreactor

Run No.	Catalyst (wt.)	Operating Conditions			
		HZSM-5/FT (or) ZMQ	Temp, °C FT	Temp, °C HZSM-5 or cat. ZMQ	H_2/CO
577-629	10% Co/Zr Base (0.1 g) + HZSM-5 (0.1 g)	1	250	250-400	1
630-680	10% Co/Zr Base (0.1 g) + HZSM-5 (0.4 g)	4	250	250-400	1,2,3
681-696	10% Co/Zr Base (0.1 g) + HZSM-5 (0.2g)	2	250	250-400	1
697-732	10% Co/Zr Base (0.1 g) + Catalyst ZMQ (0.4 g)	4	250	250-400	1
735-761	10% Co/Zr Base (0.1 g) + Catalyst ZMQ (0.1 g)	1	250	250-400	1

Table 16. Effect of Temperature of HZSM-5 reactor on product distribution

Reactor size - 1/4" OD
FT Cat. - 10% Co/Zr base
Wt of FT Cat. - 0.1 g
Wt of HZSM-5 - 0.2 g
HZSM/FT ratio - 2
Feed H_2/CO - 1

Run No.		687	688	689	690	691
Exit flow rate, mL/min		9.1	9.3	8.6	9.6	9.8
Time-on-stream, h		19.25	20.25	21.25	22.25	25.5
CO conv. %		7.0	7.2	8.0	7.3	6.9
Temp. FT Reactor, °C		250	250	250	250	250
Tem. HZSM-5 Reactor, °C		250	300	350	400	400
H.C. Analysis, wt%						
Aliphatics:	C_1	18.1	13.7	14.4	15.5	18.6
	C_2	2.4	2.3	3.7	9.5	10.8
	C_3	9.5	10.9	16.1	23.9	25.6
	C_4	20.6	20.1	20.9	18.9	20.0
	C_5^+	28.1	16.4	9.2	5.4	5.6
Aromatics:	A_6	0.4	0.8	1.8	2.3	2.4
	A_7	2.0	6.1	7.4	6.9	7.2
	A_8	7.0	10.0	6.8	6.2	6.4
	A_9	4.4	4.6	1.7	1.2	1.1
	A_{10}^+	7.4	15.4	17.9	10.2	2.3
Total Arom, wt%		21.2	36.9	35.6	26.8	19.4
$C_2^=/$Total C_2, %		24.1	51.7	59.8	73.2	73.2
$C_3^=/$Total C_3, %		25.0	21.9	17.3	23.7	24.9
$iC_4^-/$Total C_4, %		38.2	61.9	64.5	56.1	56.1
Total C_5^+ (incl. Arom.)		49.3	53.3	44.8	32.2	25.0

Talbe 17. Effect of Temperature of HZSM-5 Reactor on Product Distribution

Reactor size - 1/4" OD
FT catalyst - 10% Co/Zr base
Wt. of FT Cat. - 0.1005 g
Wt. of HZSM-5 - 0.1004 g
HZSM-5/FT - 1
Feed H_2/CO - 1

Run No.		585	591	602	608	613	616	617
Exit flow rate,mL/min		9.9	10.5	10.5	10.3	11.6	10.6	10.3
Time-on-stream, h		20.5	46.0	86.5	128.5	152.5	180.5	182.5
CO conv. %		7.6	4.3	5.6	2.7	1.8	2.1	5.9
Temp. FT reactor, °C		250	250	250	250	250	250	250
Temp. HZSM-5 reactor, °C		250	275	300	325	350	375	400
H.C. Analysis, wt%								
Aliphatics	C_1	16.4	19.2	21.0	21.7	22.4	23.4	22.2
	C_2	3.0	3.9	5.6	7.9	11.5	13.0	17.1
	C_3	11.2	12.0	15.2	18.9	23.8	25.1	28.0
	C_4	25.0	23.5	24.3	23.4	21.6	17.8	15.7
	C_5^+	33.5	23.8	18.1	14.1	11.1	7.5	5.5
Aromatics	A_6	0.5	0.3	0.6	0.8	0.9	0.9	1.0
	A_7	1.1	2.8	3.5	4.3	3.6	3.0	2.8
	A_8	4.0	6.7	6.0	5.7	4.3	3.6	3.0
	A_9	2.4	4.1	3.0	1.9	0.6	0.6	0.4
	A_{10}^+	2.9	3.6	3.2	1.4	0.3	5.0	4.3
Total Arom., wt%		10.9	17.5	16.3	14.1	9.7	13.2	11.5
$C_2^=$/Total C_2, %		49.3	60.0	70.3	74.8	79.7	82.9	84.2
$C_3^=$/Total C_3, %		64.2	49.1	57.1	60.5	67.0	68.4	69.6
i-C_4/Total C_4, %		17.1	46.2	49.2	47.7	40.9	37.3	33.5
Total C_5^+(incl. Arom.)		44.4	41.3	34.0	28.2	20.8	20.7	17.0

Table 18. Effect of Temperature of HZSM-5 Reactor on Product Distribution

Reactor size - 1/4" OD
FT Catalyst - 10% Co/Zr Base
Wt. of FT Cat. - 0.1000 g
Wt. of HZSM-5 - 0.3999 g
HZSM-5/FT - 4
Feed H_2/CO - 1

Run No.		644	676	677	678
Exit flow rate, mL/min		9.4	8.2	7.9	7.4
Time-on-stream, h		46.75	215.5	217.0	218.25
CO conv. %		7.0	3.5	2.9	3.7
Temp. FT Reactor, °C		250	250	250	250
Temp. HZSM-5 reactor, °C		250	300	350	400
H.C. Analysis, wt%					
Aliphatics	C_1	17.8	17.2	19.5	22.5
	C_2	2.2	—	4.2	11.6
	C_3	9.0	10.6	17.6	27.0
	C_4	19.2	16.0	17.9	27.0
	C_5+	22.1	10.7	6.5	3.3
Aromatics	A_6	0.3	1.4	1.7	2.1
	A_7	3.2	8.7	6.1	5.8
	A_8	7.9	10.7	5.8	4.9
	A_9	4.8	3.3	1.0	0.4
	$A_{10}+$	13.6	21.6	19.7	5.8
Total Arom., wt%		29.8	45.7	34.3	19.0
$C_2=$/Total C_2, %		26.6	48.1	61.5	70.0
$C_3=$/Total C_3, %		16.1	14.2	13.4	17.2
i-C_4/Total C_4, %		59.0	67.0	64.9	57.7
Total C_5+ (incl. Arom.)		51.9	56.4	40.8	22.3

Table 19. Effect of Temperature of Catalyst ZMQ Reactor on Product Distribution

Reactor Size - 1/4"OD
FT Cat. - 10% Co/Zr Base
Wt. FT Cat. - 0.1 g
Wt. Cat. ZMQ - 0.4 g
Feed H_2/CO - 1

Run No.		706	714	717	722	731
Exit flow rate, mL/min		4.9	4.7	4.6	4.2	4.1
Time-on-stream, h		23.5	47.5	53.5	68.5	95.25
CO conv. %		11.6	10.3	10.7	11.1	8.4
Temp. FT reactor, °C		250	250	250	250	250
Temp. Cat. ZMQ reactor, °C		250	275	300	350	400
H.C. Analysis, wt%						
Aliphatics	C_1	17.8	20.7	19.4	18.4	18.5
	C_2	2.7	2.7	4.1	4.9	6.2
	C_3	7.4	11.3	15.0	22.1	26.8
	C_4	19.8	23.4	25.0	25.1	23.5
	C_5^+	43.7	35.8	32.0	25.1.	21.1
Aromatics	A_6	0.5	0.6	0.6	0.5	0.4
	A_7	1.1	0.6	0.0	0.2	0.0
	A_8	4.3	3.1	2.4	2.0	1.9
	A_9	2.7	1.9	1.5	1.6	1.5
Total Arom., Wt %		8.6	6.2	4.5	4.3	3.8
C_2=/Total C_2, %		39.8	48.2	52.2	62.2	72.6
C_3=/Total C_3, %		76.0	82.3	85.8	90.8	92.8
i-C_4/Total C_4, %		12.4	11.7	9.7	6.3	4.3
Total C_5^+ (incl. Arom.)		52.3	42.0	36.5	29.4	25.0

Table 20. Effect of Temperature of Cat. ZMQ Reactor on Product Distribution

Reactor size - 1/4"
FT catalyst - 10% Co/Zr base
Wt. of FT Cat. - 0.1003 g
Wt. of ZMQ - 0.1004 g
Cat. ZMQ/FT - 1
Feed H_2/CO - 1

Run No.		742	752	754	757	761
Exit flow rate, mL/min		5.3	5.6	5.7	5.7	6.7
Time-on-stream, h		19.5	47.5	52.8	61.5	76.8
CO conv. %		8.2	6.6	8.1	6.1	3.3
Temp. FT reactor, °C		250	250	250	250	250
Temp. Cat. ZMQ reactor, °C		250	275	300	350	400
H.C. Analysis, wt%						
Aliphatics	C_1	23.0	24.2	25.4	25.7	24.2
	C_2					
	C_3	9.9	12.6	14.0	18.0	20.7
	C_4	19.2	20.4	21.4	20.4	19.1
	C_5^+	40.8	40.0	36.7	33.8	33.8
Aromatics	A_6	0.4	0.2	0.2	0.2	0.2
	A_7	0.5	0.2	0.2	0.1	0.1
	A_8	1.2	1.1	1.0	0.7	0.8
	A_9	5.1	1.3	1.1	1.0	1.0
Total Arom., wt%		7.1	2.8	2.5	2.1	2.2
$C_2^=$/Total C_2, %		62.0	67.1	65.5	69.8	77.4
$C_3^=$/Total C_3, %		91.3	91.6	91.8	94.8	96.0
i-C_4/Total C_4, %		1.7	1.5	1.8	1.4	1.0
Total C_5^+ (incl. Arom.)		47.9	42.8	39.2	35.9	36.0

Table 21. Comparison of the product distributions obtained using various Cat ZMQ/FT ratios

Run No.		742	706
Cac ZMQ/FT		1	4
Exit flow rate, mL/min		5.3	4.9
Time-on-stream, h		19.5	23.5
CO conv. %		8.2	11.6
Temp. FT reactor, ^{o}C		250	250
Temp. Cat. ZMQ reactor, ^{o}C		250	250
H.C. Analysis, wt%			
Aliphatics	C_1	18.9	17.8
	C_2	4.1	2.7
	C_3	9.9	7.4
	C_4	19.2	19.8
	C_5+	40.8	43.7
Aromatics	A_6	0.4	0.5
	A_7	0.5	1.1
	A_8	1.2	4.3
	A9	5.1	2.7
Total Arom., wt%		7.1	8.6
C_2=/Total C_2, %		62.0	39.8
C_3=/Total C_3, %		91.3	76.0
i-C_4/Total C_4, %		1.7	12.4
Total C_5+ (incl. Arom.)		47.9	52.3

Table 22. Comparison of Product Distributions Obtained When Using HZSM-5 and Catalyst ZMQ

Run No.		638	706
Zeolite used		HZSM-5	CATALYST ZMQ
Wt. 10% Co/Zr Base		0.1000	0.1000
Wt. Zeolite		0.3999	0.4000
Exit flowrate, mL/min		8.5	4.9
Time-on-stream, h		22.5	23.5
CO conv. %		9.8	11.6
Temp. FT reactor, °C		250	250
Temp. Zeolite reactor, °C		250	250
H.C. Analysis, wt%			
Aliphatics	C_1	16.0	17.8
	C_2	2.1	2.7
	C_3	9.6	7.4
	C_4	20.6	19.8
	C_{5}^{+}	24.5	43.7
Aromatics	A_6	0.3	0.5
	A_7	3.3	1.1
	A_8	8.4	4.3
	A_9	5.2	2.7
	A_{10}^{+}	10.0	0.0
Total Arom., wt%		27.2	8.6
$C_2^=$/Total C_2, %		22.3	39.8
$C_3^=$/Total C_3, %		14.1	76.0
i-C_4/Total C_4, %		57.9	12.4
Total C_{5+} (incl. Arom.)		51.6	52.3

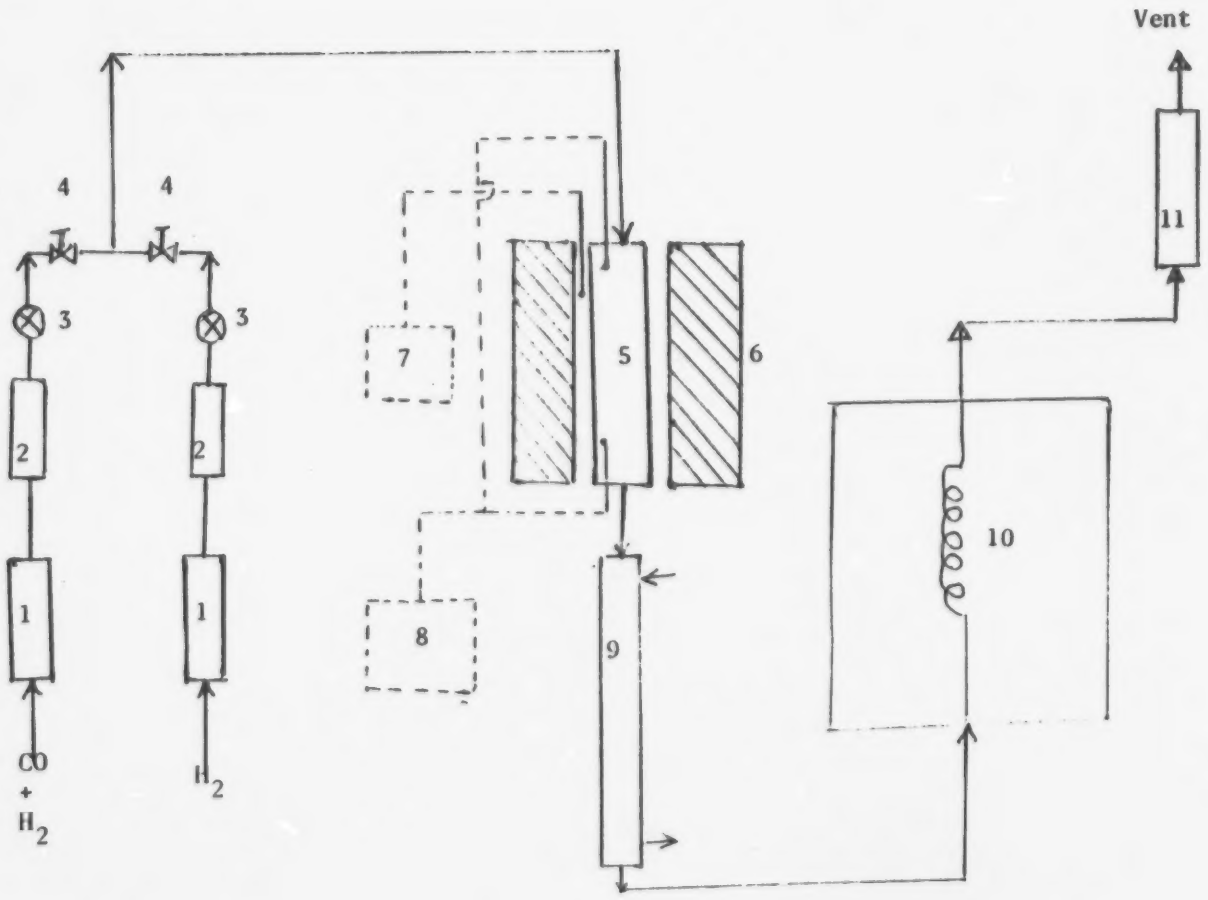


Figure 1. Apparatus for carbon monoxide hydrogenation. (1) Gas Purifier (2) Flow Meter (3) Shut-off Valves (4) Needle Valve (5) Reactor (6) Furnace (7) Temperature Controller-Indicator (8) Multi-Channel Temperature Indicator (9) Condenser (10) GC System (11) Bubble Flow Meter

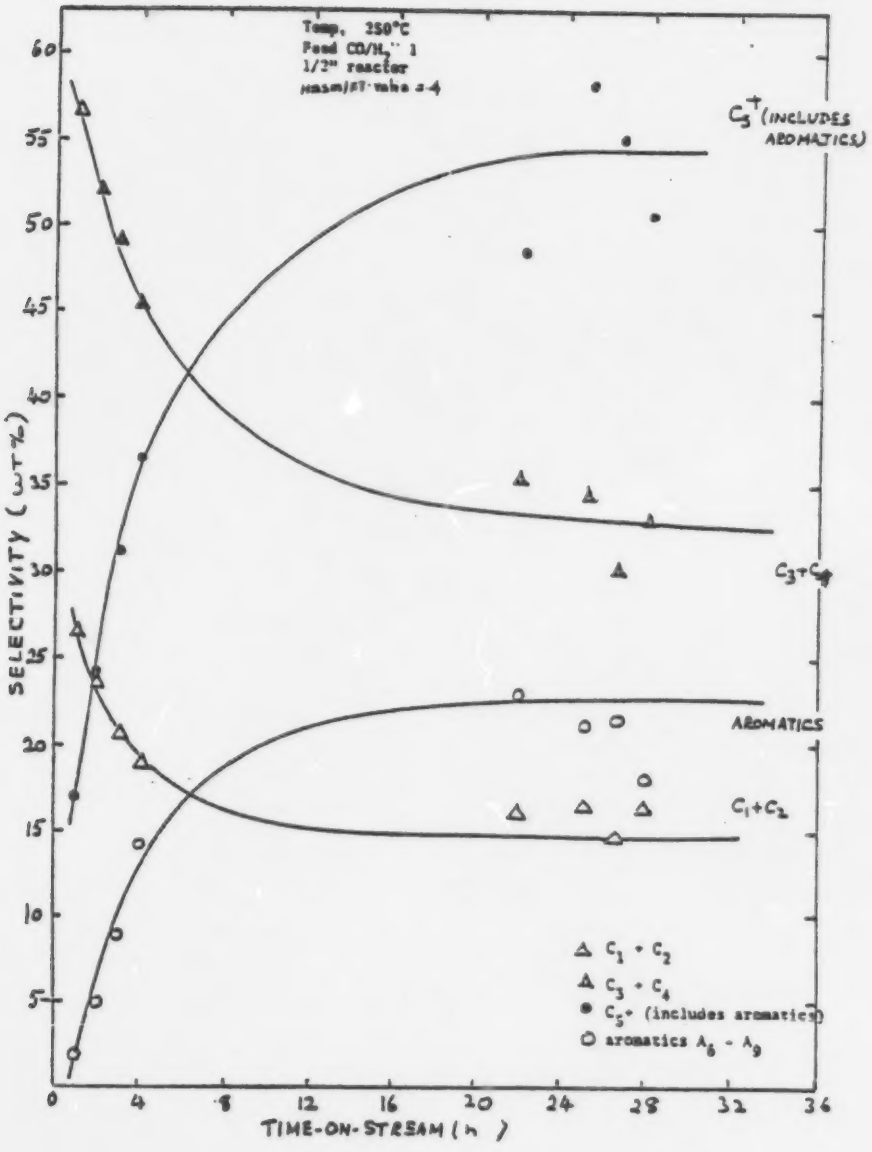


Figure 2. Product Distribution with Time-on-stream.

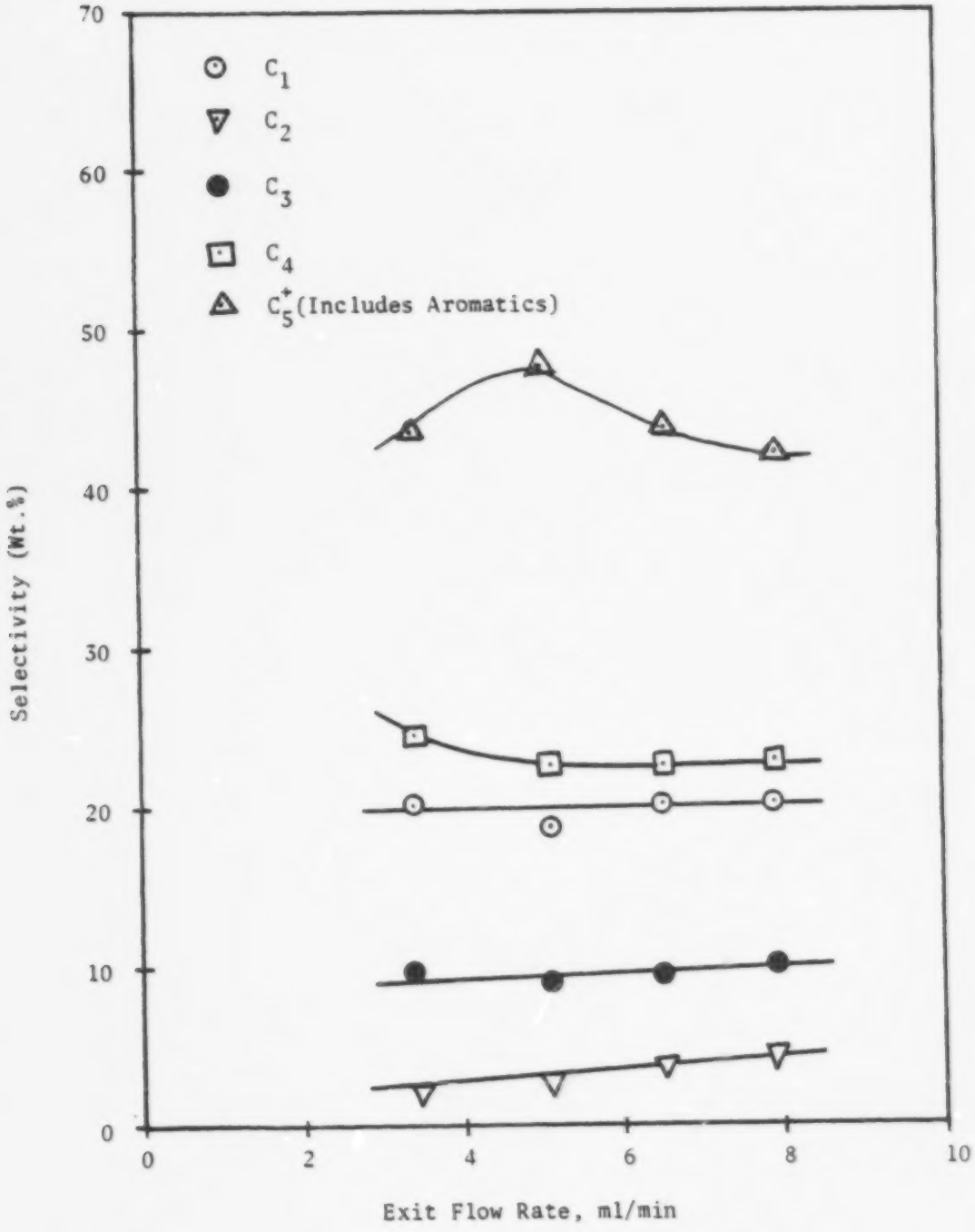


Figure 3. Effect of Flowrate on the Product Distribution

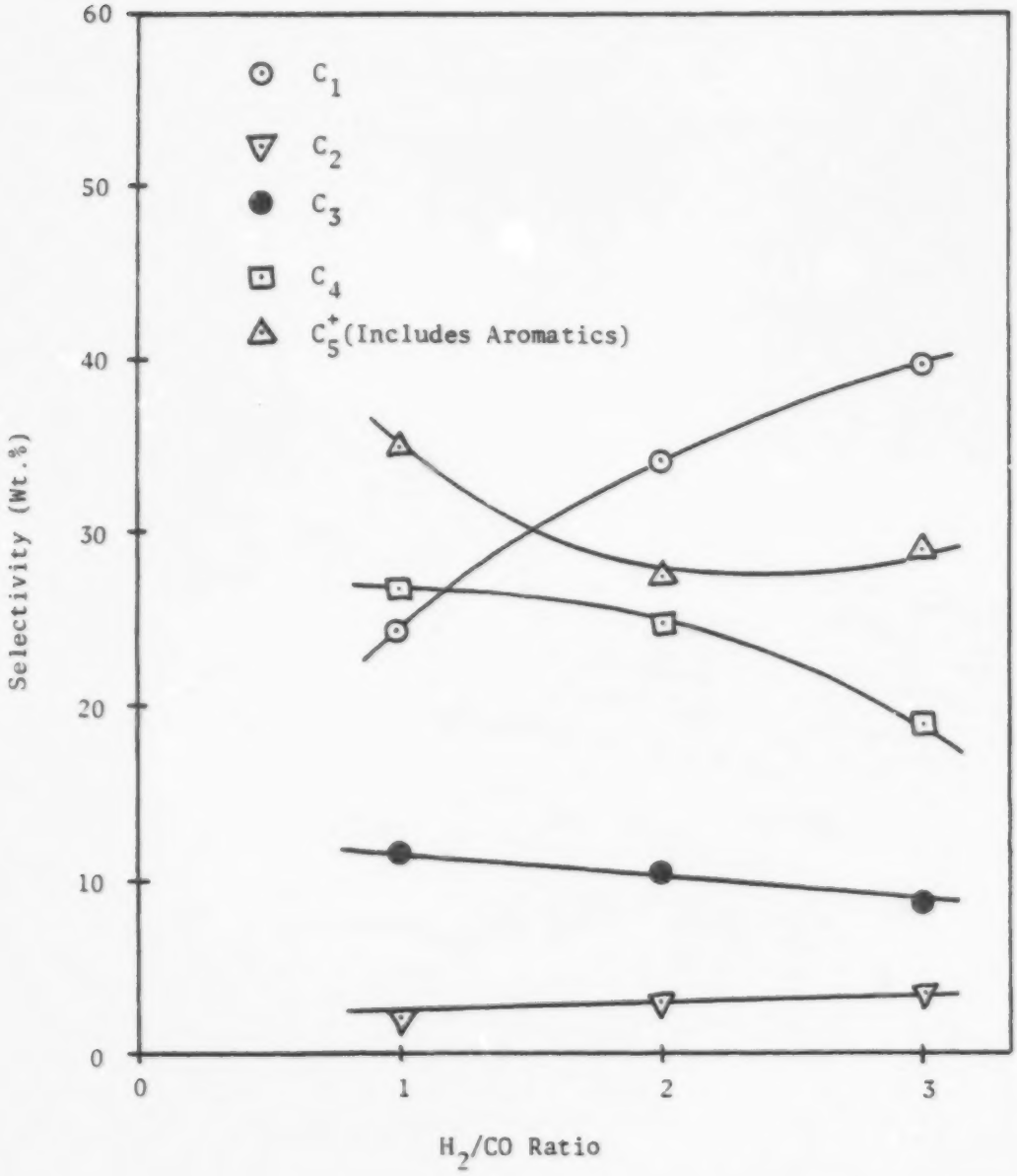


Figure 4. Effect of Feed Composition on Product Distribution

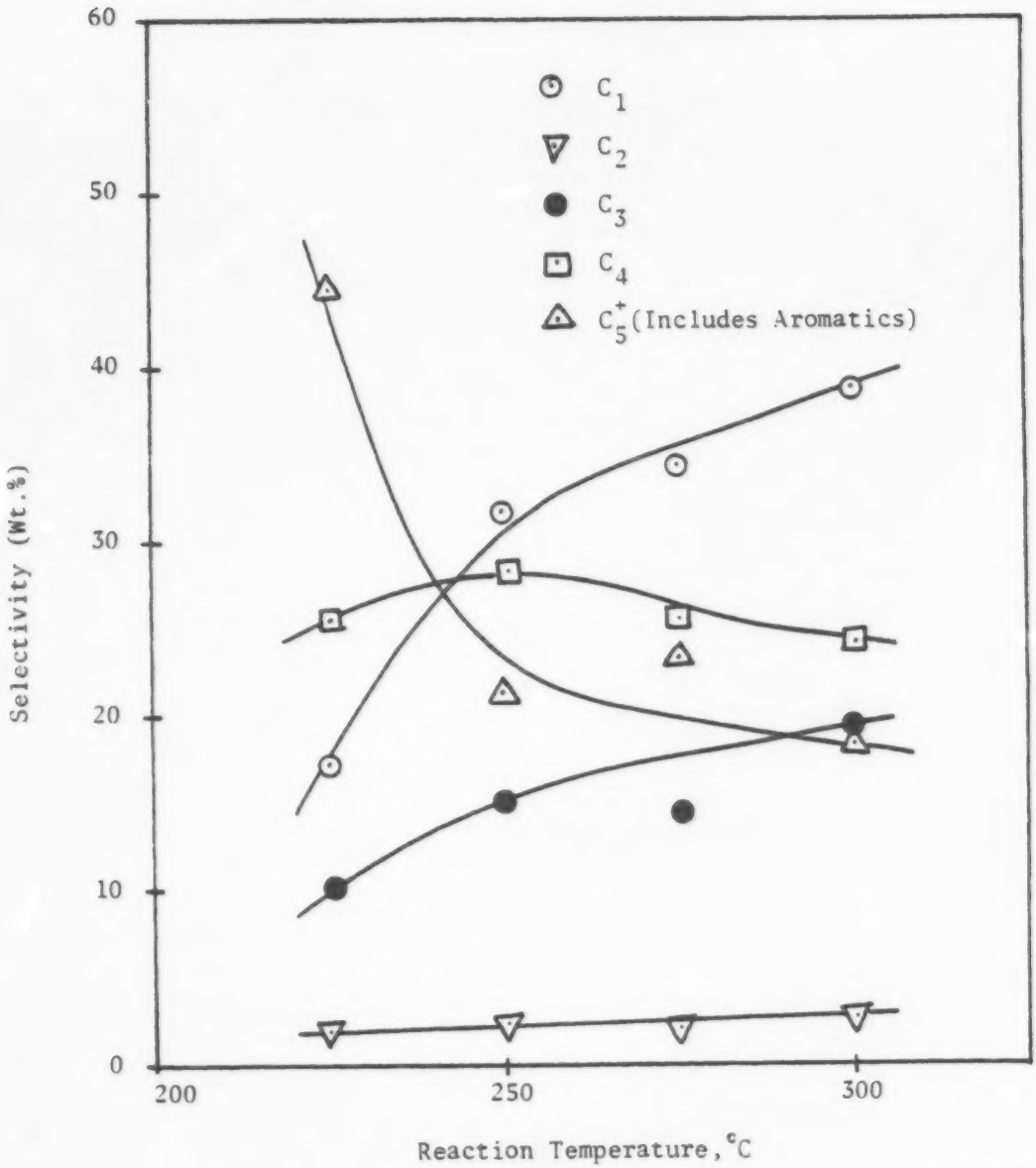


Figure 5. Effect of Reaction Temperature on Product Distribution

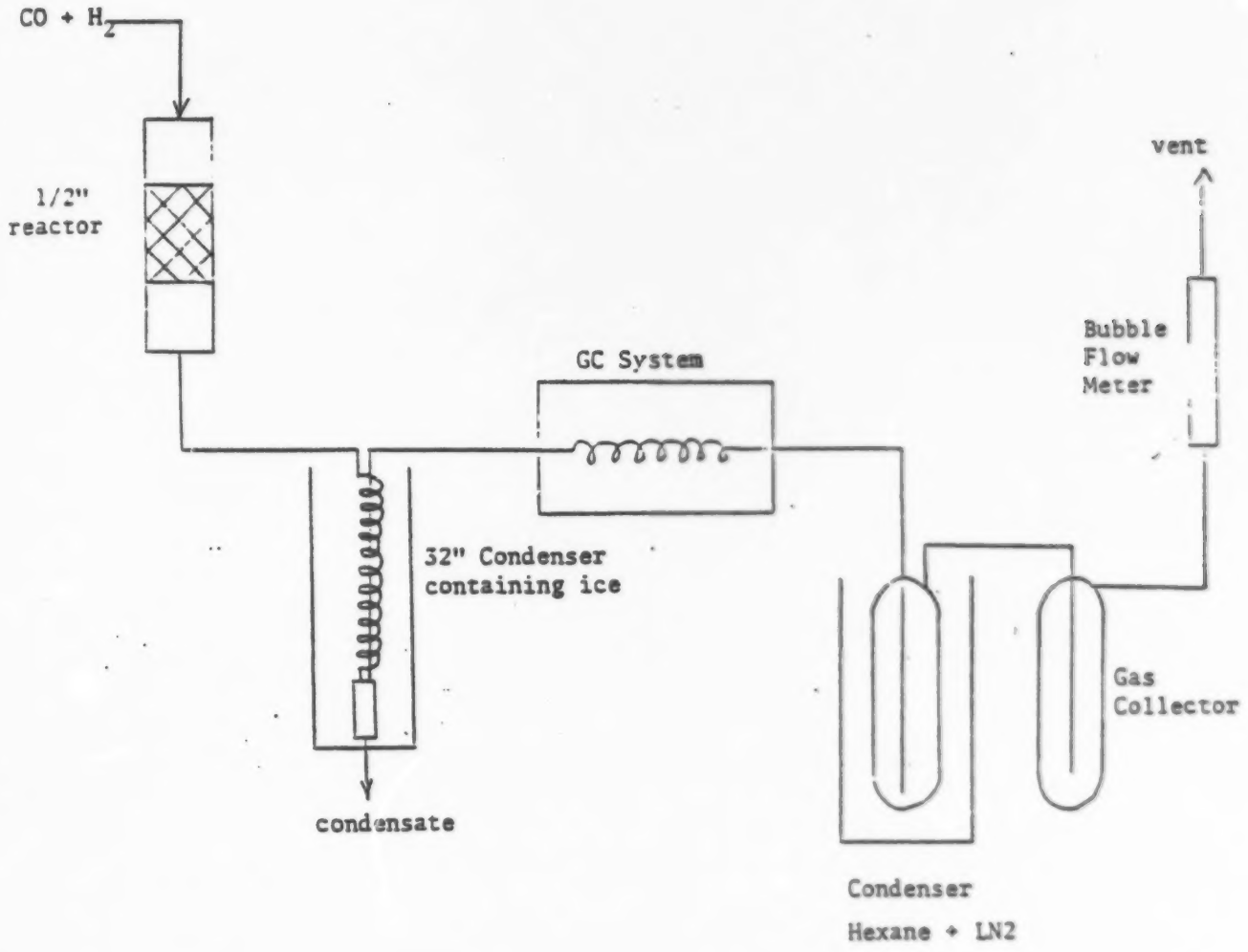


Figure 6. Schematic Diagram of the GC/Condenser System

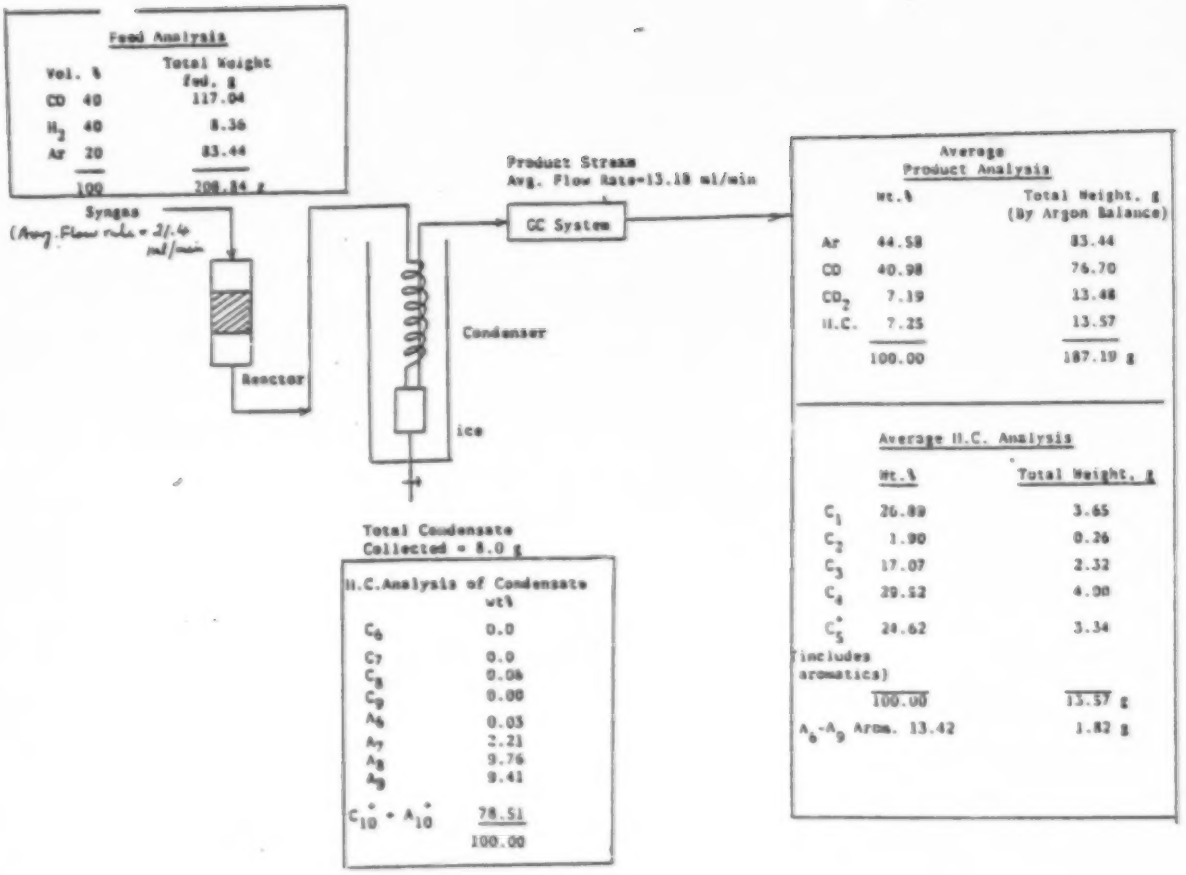


Figure 7. Overall Material Balance

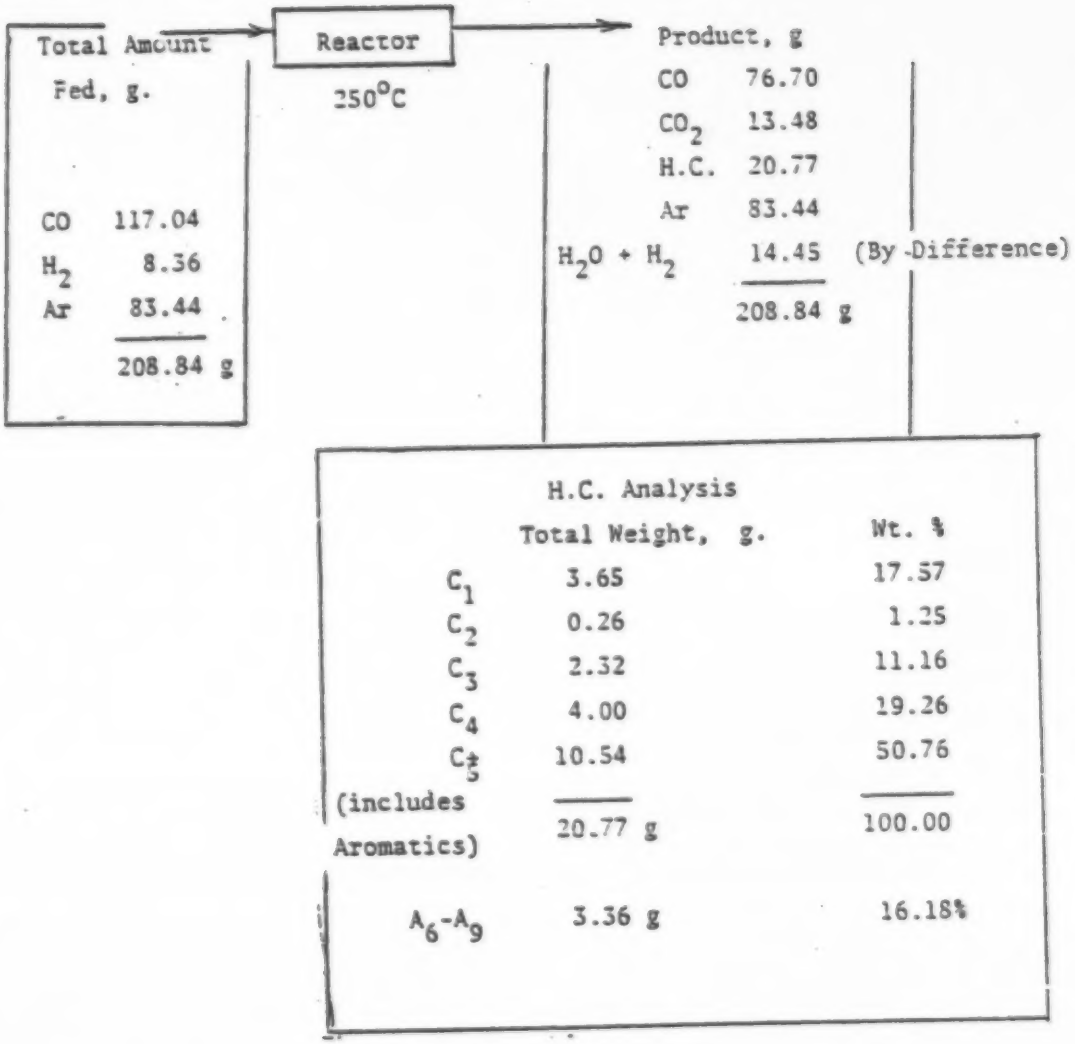


Figure 8. Overall Material Balance Assuming the Condensate Contains 90% Hydrocarbons.

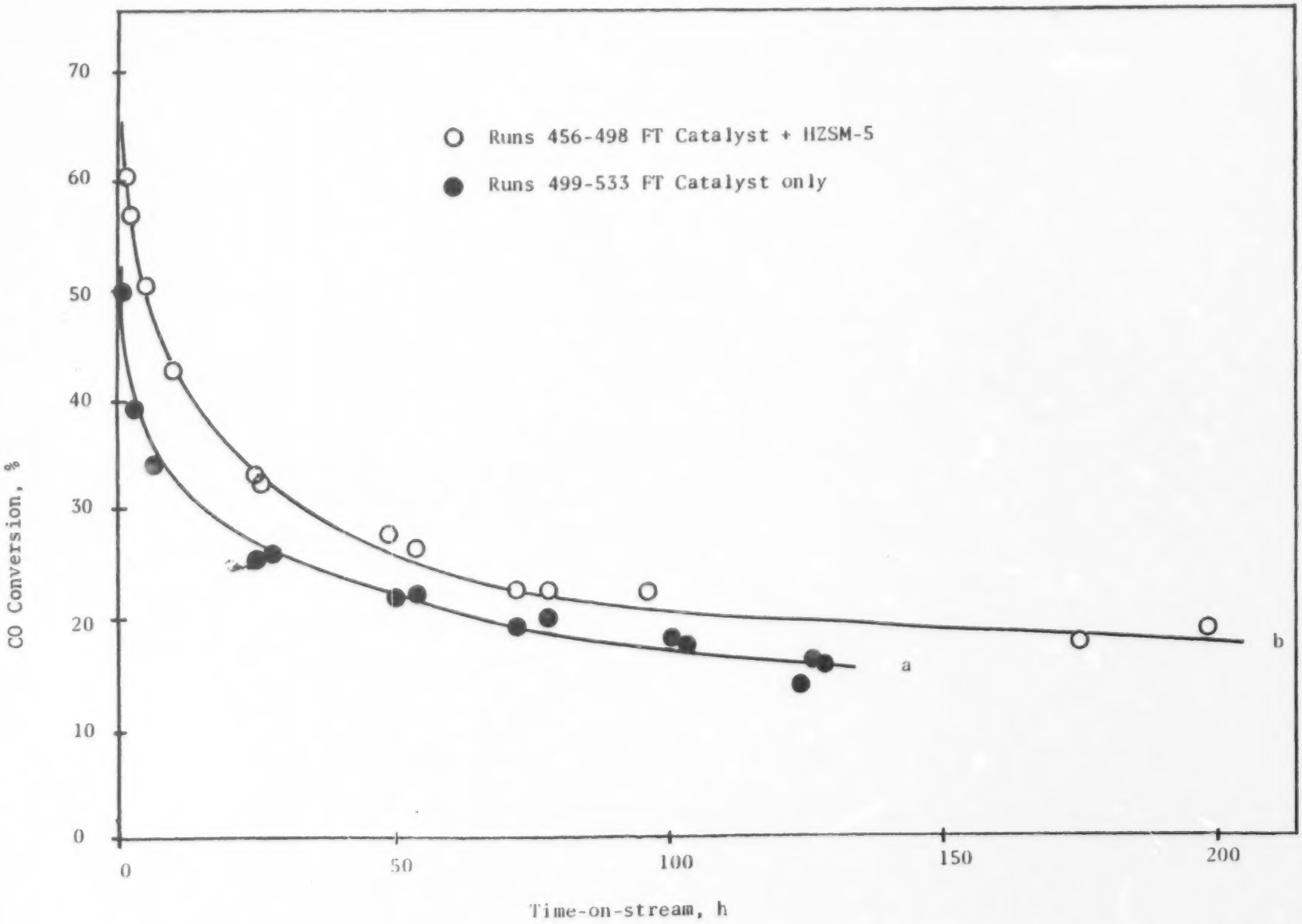


Figure 9. Variation of Carbon Monoxide Conversion with Time-on-stream

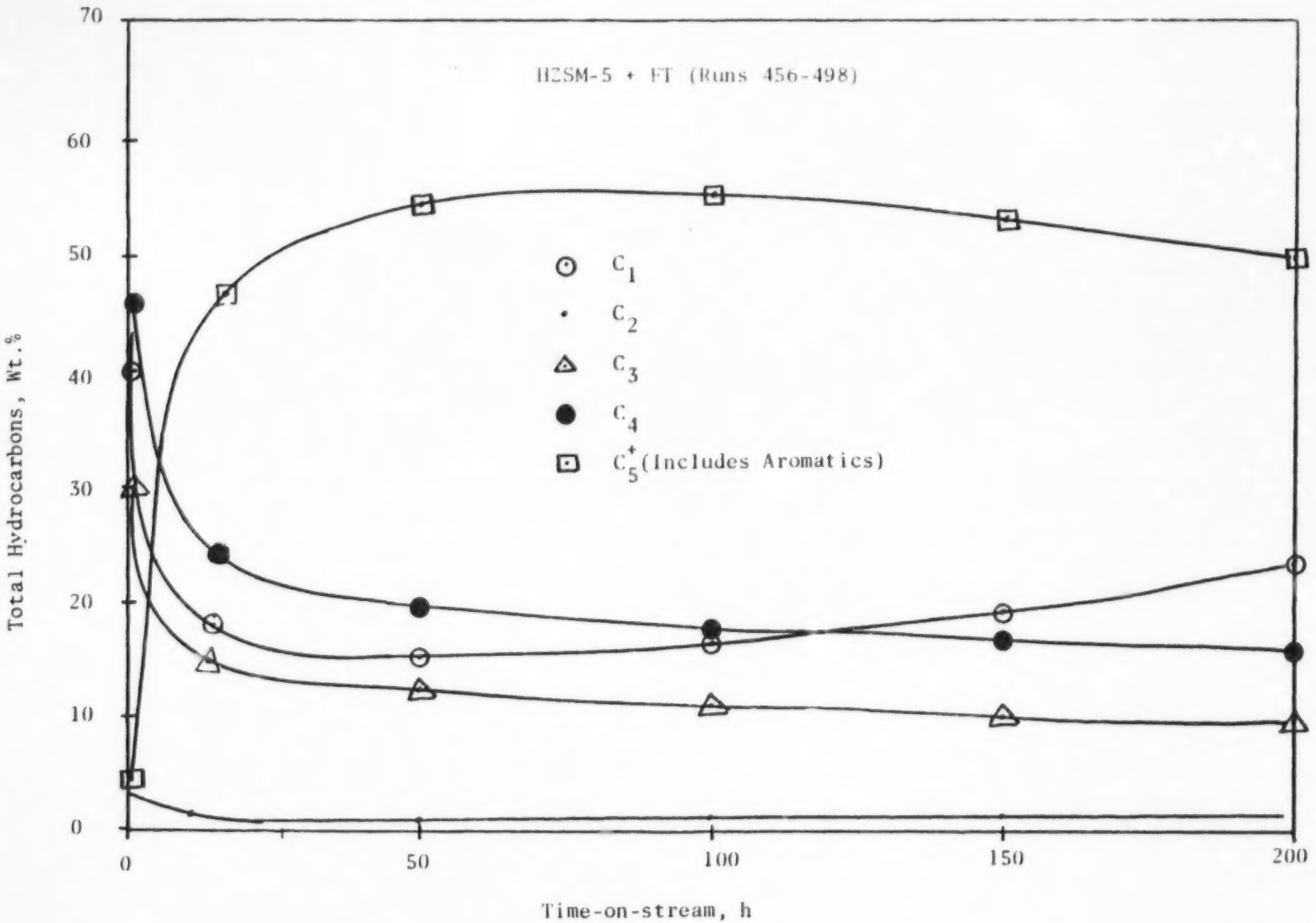


Figure 10. Variation of Product Distribution with Time-on-stream

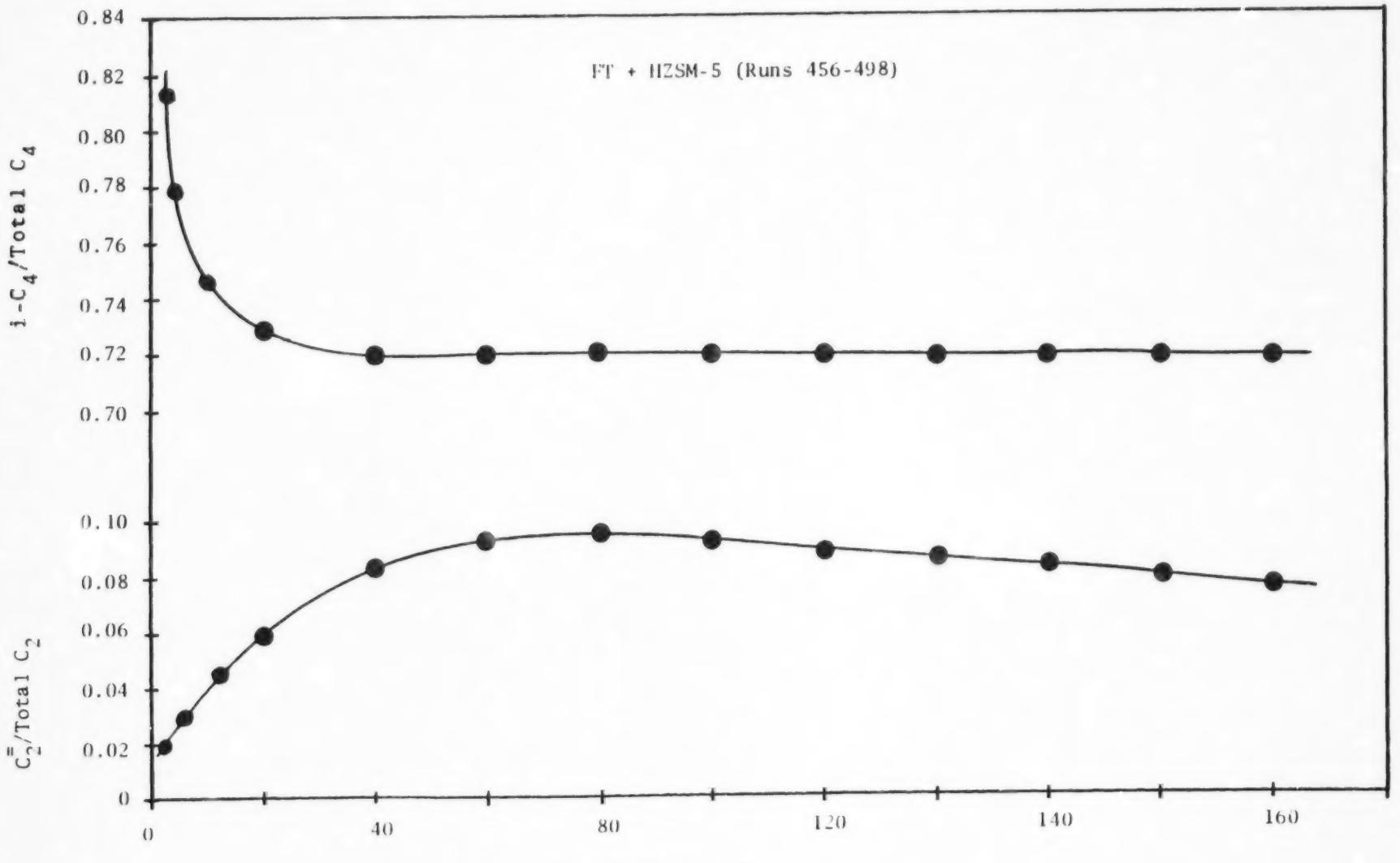


Figure 11. Variation of $C_2^=/C_2$ and i-C_4/C_4 Fractions with Time-on-stream.

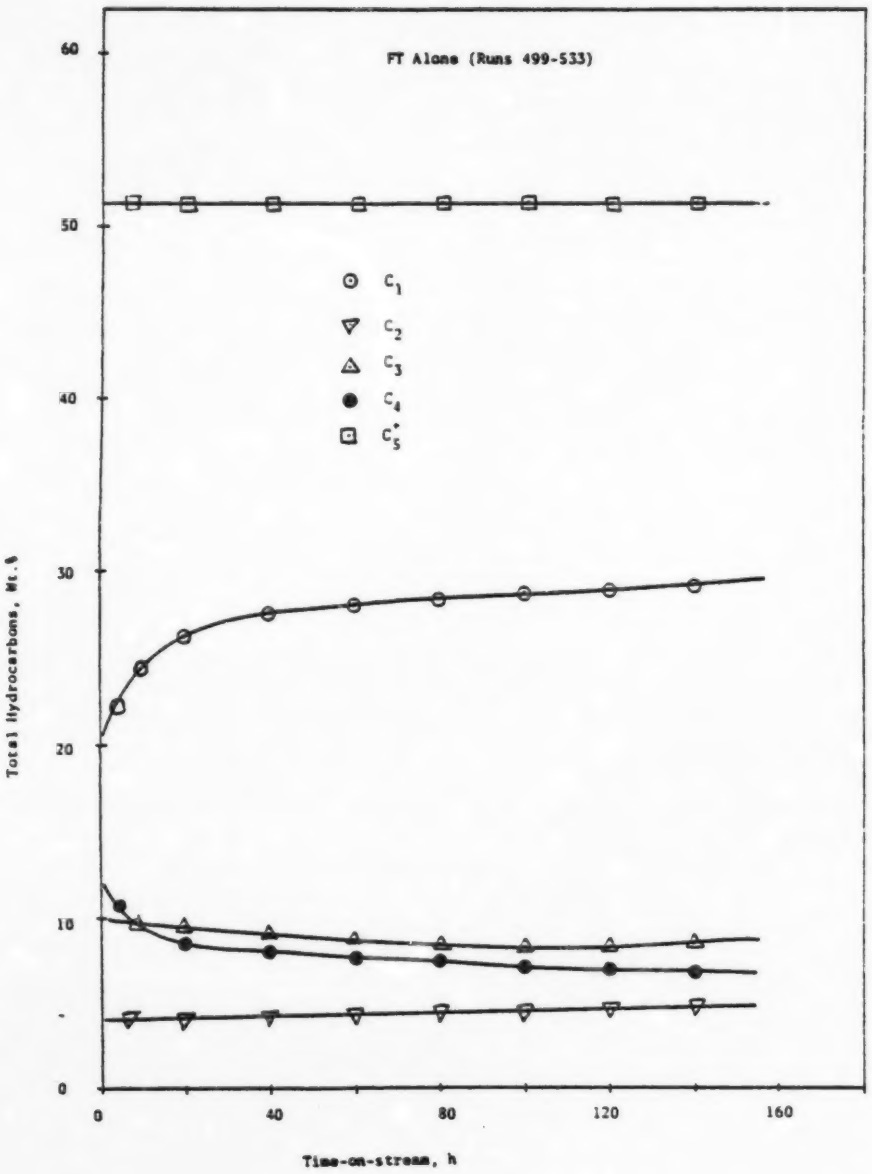


Figure 12. Variation of Product Distribution with Time-on-stream.

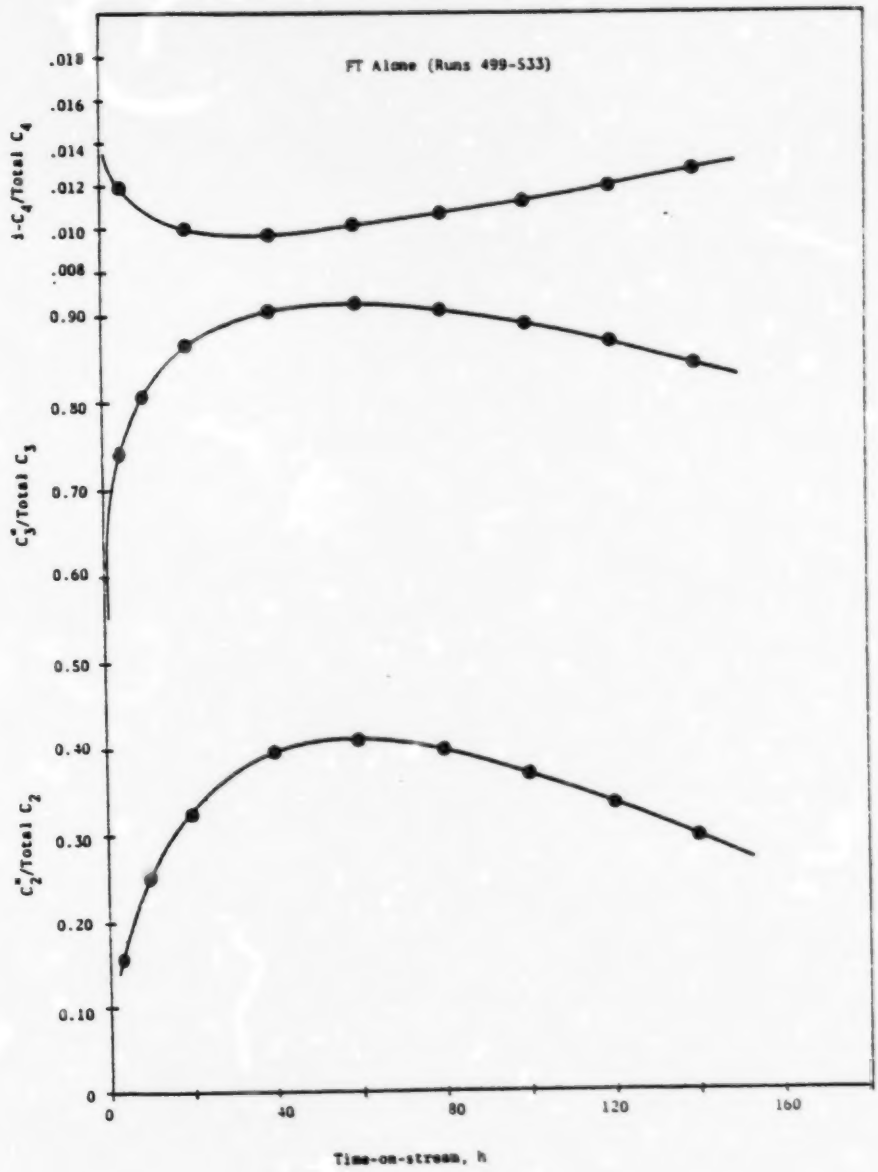


Figure 13. Variation of Olefinicity with Time-on-stream.

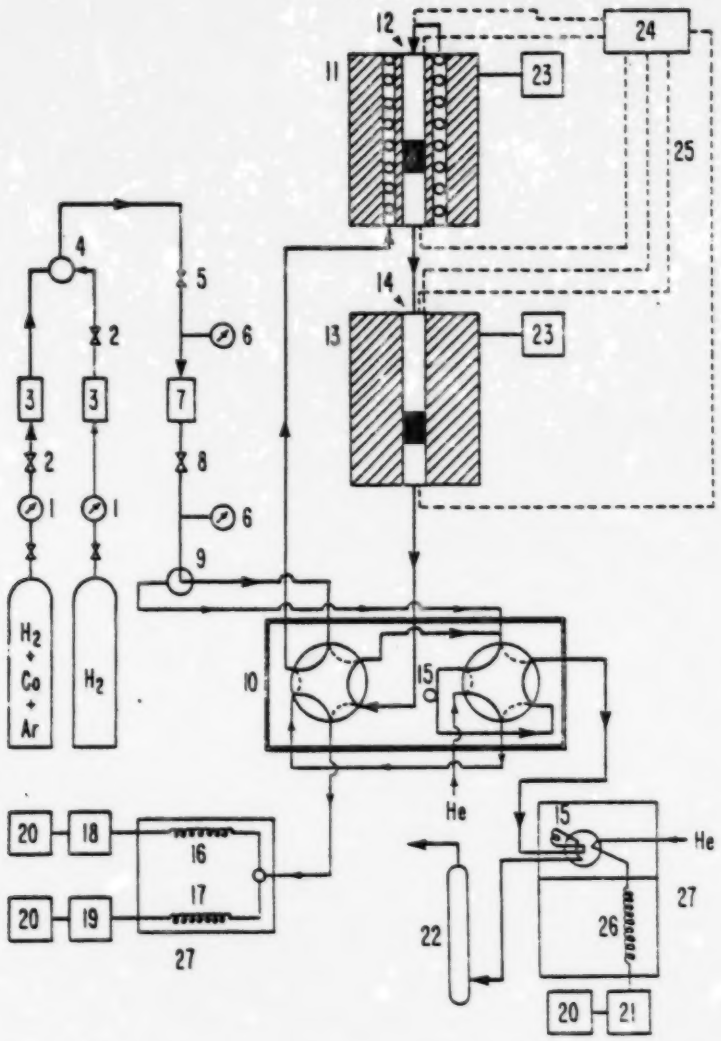


Figure 14. Schematic Diagram of Dual Bed Reactor and Analytical System(1) Pressure Guage (2) Valve (3) Gas Purifier (4) 3-Way Valve (5) Needle Valve (6) Pressure Guage (7) Mass Flow Transducer (8) Micro-metering Valve (9) 3-Way Valve (10) Valve Switching Chamber (11) FT Reactor Furnace (12) FT Reactor (13) HZSM-5 Reactor Furnace (14) HZSM-5 Reactor (15) Sample Loop (16) Chromosorb 102 Column (17) Carbosieve 'S' Column (18) FID (19) TCD (20) Integrator (21) FID - HP5880A (22) Bubble Flow Meter (23) Temp. Controller (24) Temp. Indicator (25) Thermocouples (26) 10% SE-30 OV-101 Column (27) GC Oven

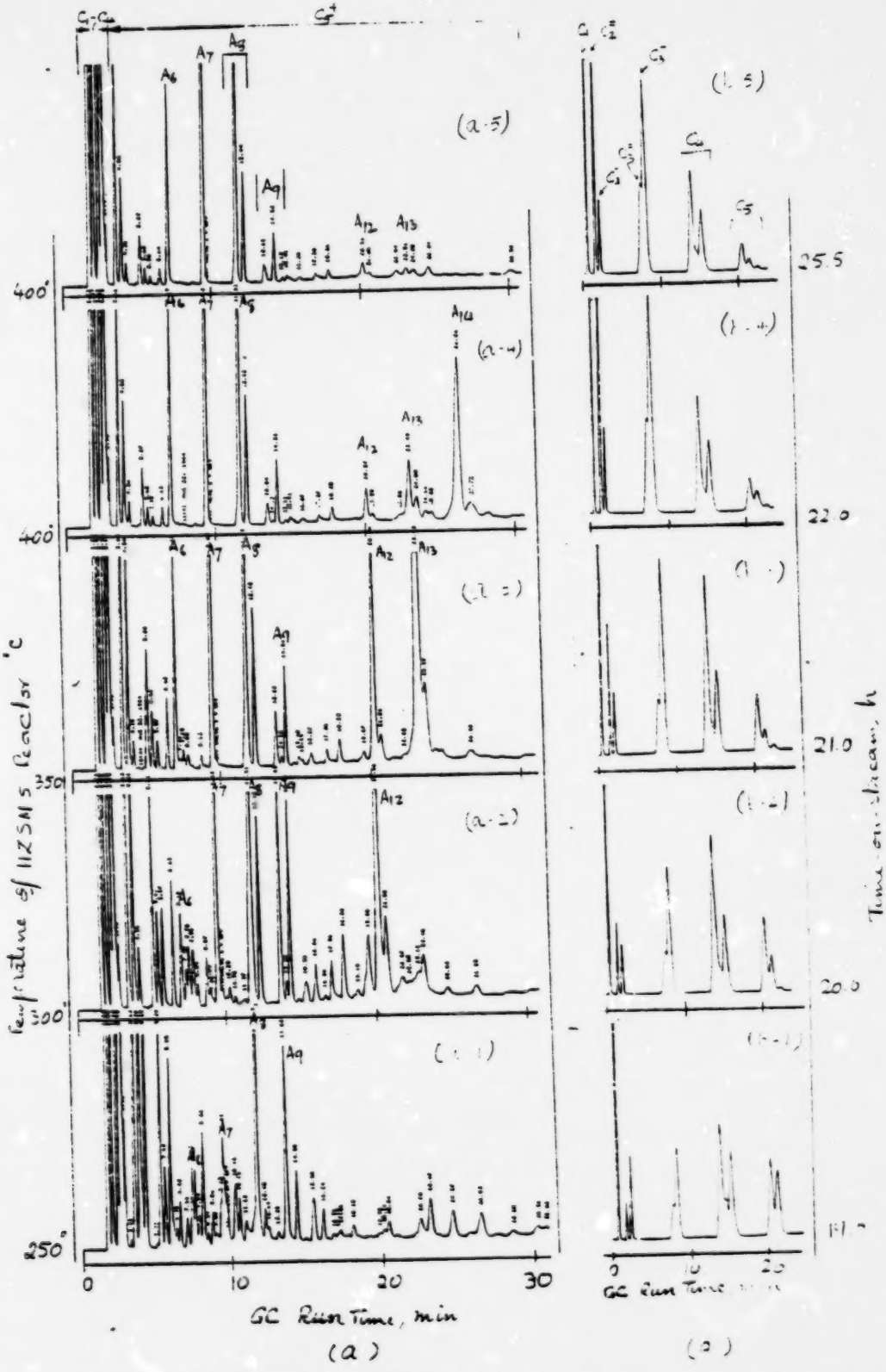
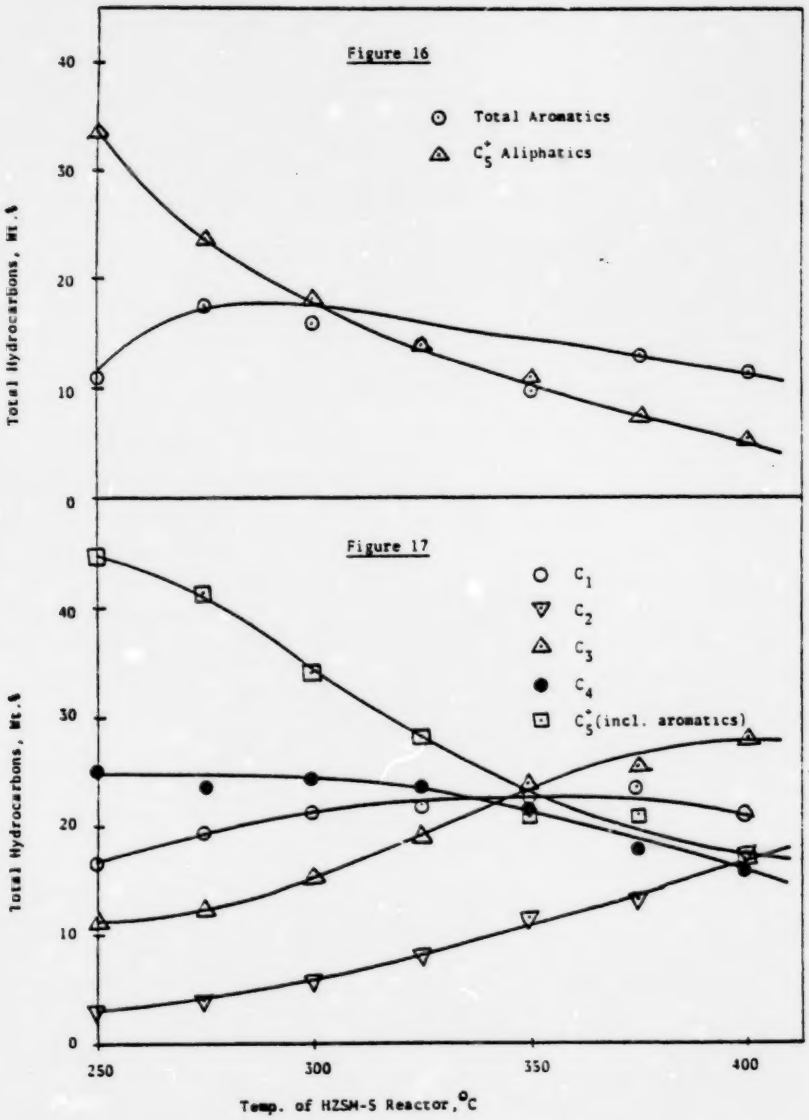
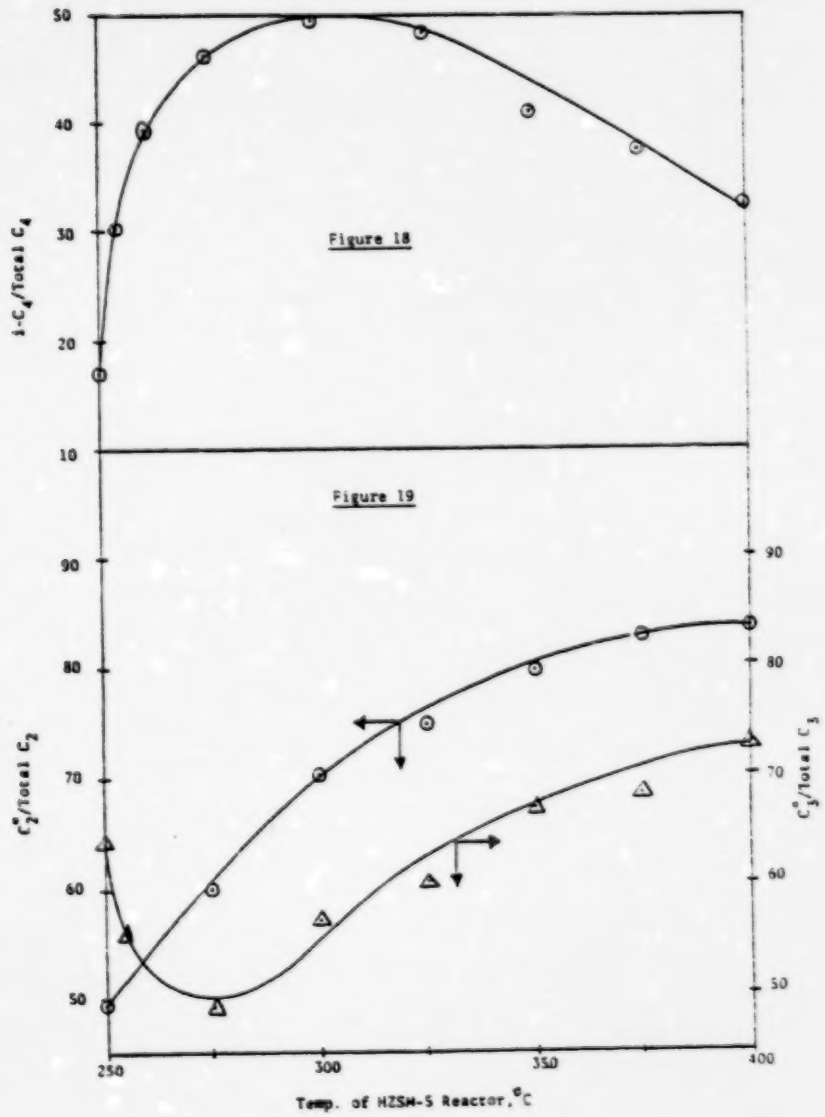


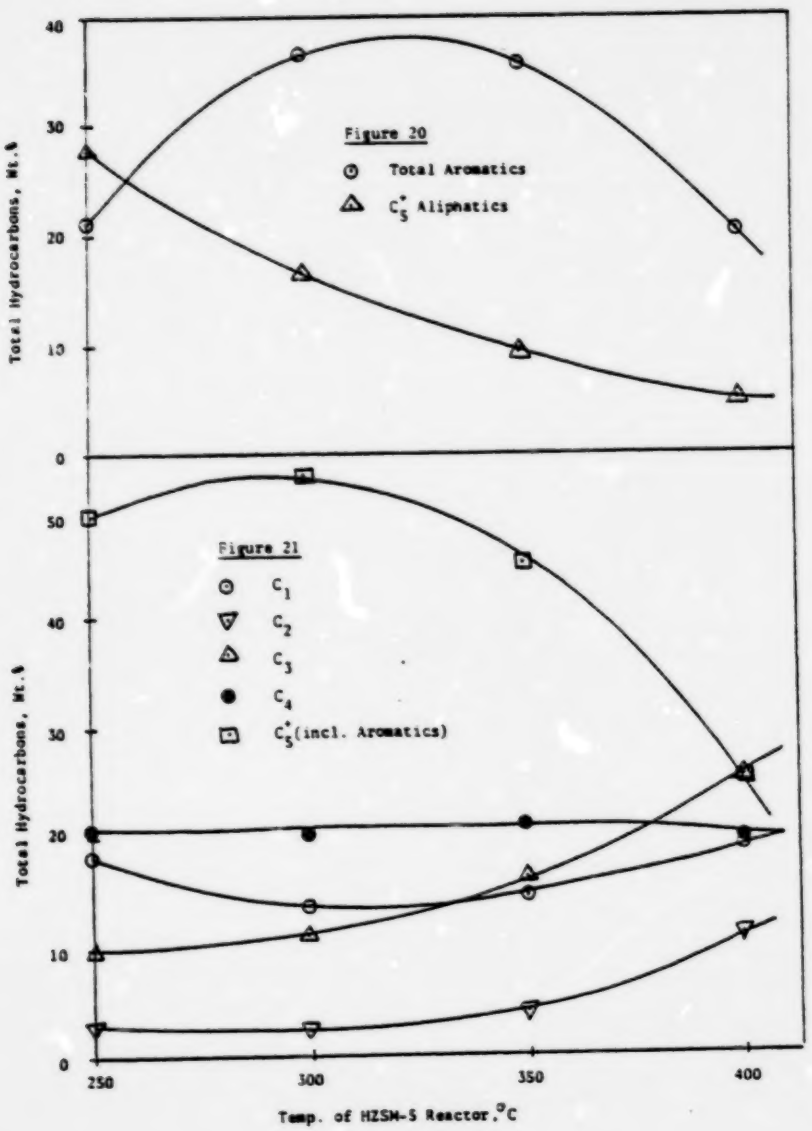
Fig. 4.4. A comparison of chromatograms at varying temperature of HZSM-5 reactor. G.C. Columns: (a) 10% OV-101on Chromosorb W HP, (b) Chromosorb 102. HZSM-5/FT ratio=2; $H_2/CO=1$.



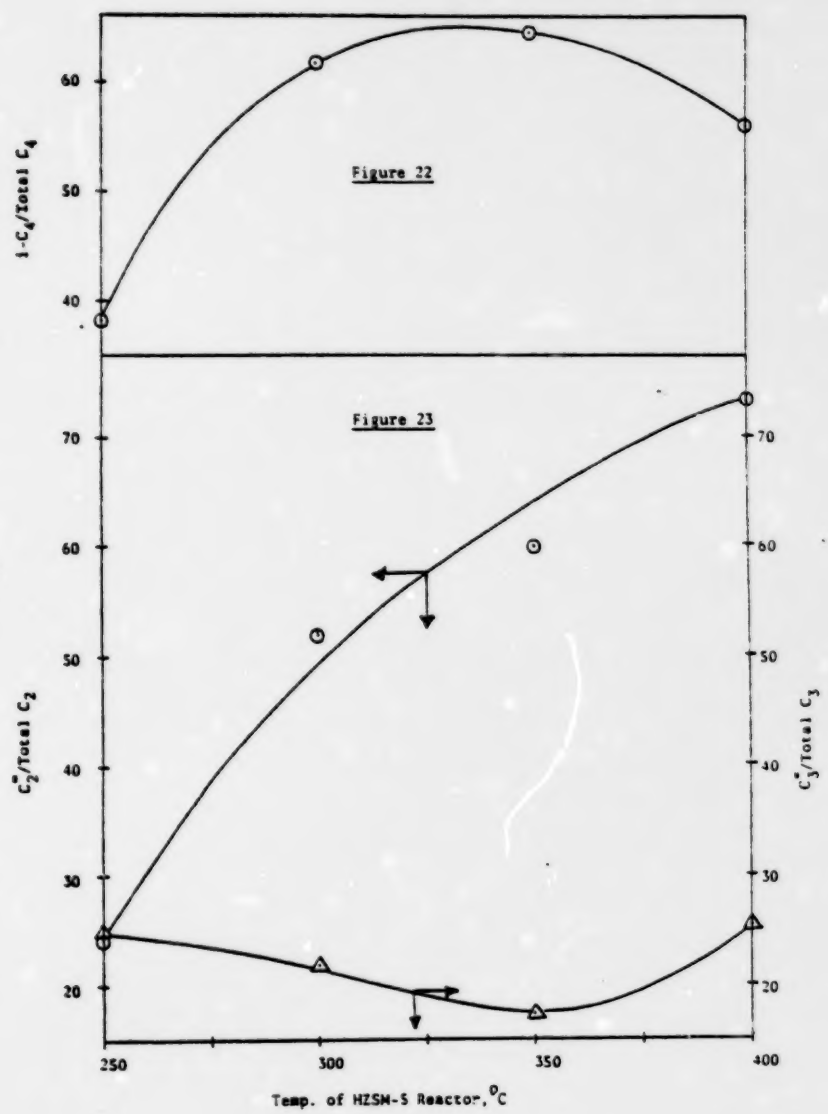
Figures 16 & 17. Variation of Product Distribution with temperature of HZSM-5 Reactor, HZSM-5/FT=1



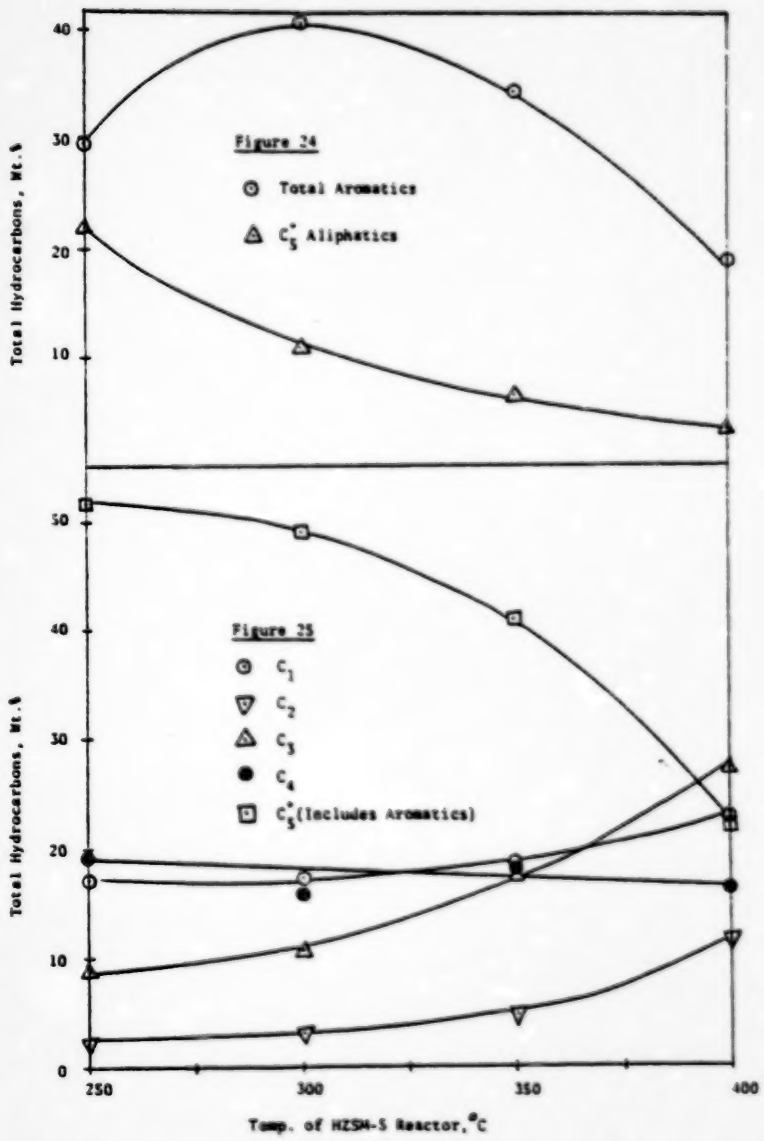
Figures 18 & 19. Variation of C_2-C_4 Distribution with Temperature of HZSM-5 Reactor, HZSM-5/FT=1



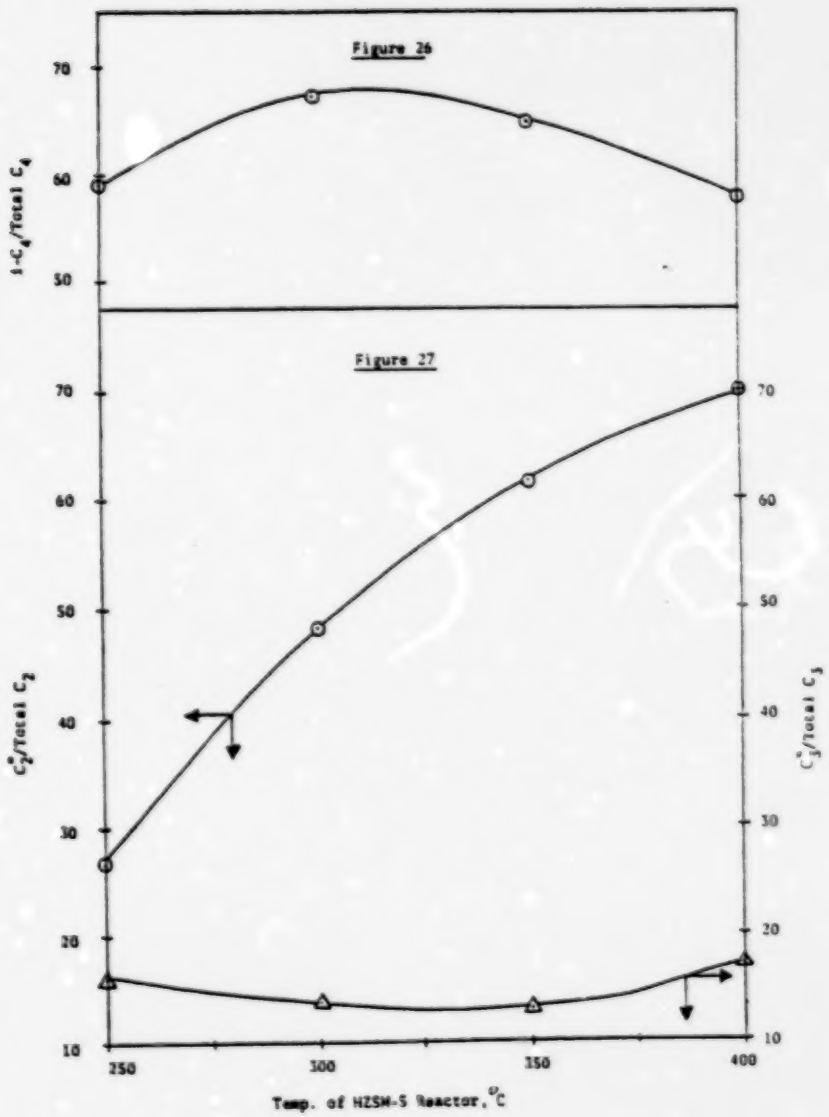
Figures 20 & 21. Variation of Product Distribution with Temperature of HZSM-5 Reactor, HZSM-5/FT=2



Figures 22 & 23. Variation of C_2-C_4 Distribution with Temperature of HZSM-5 Reactor, HZSM-5/FT=2



Figures 24 & 25. Variation of Product Distribution with Temperature of HZSM-5 Reactor, HZSM-5/FT=4



Figures 26 & 27. Variation of C_2-C_4 Distribution with Temperature of HZSM-5 Reactor, HZSM-5/FT=4

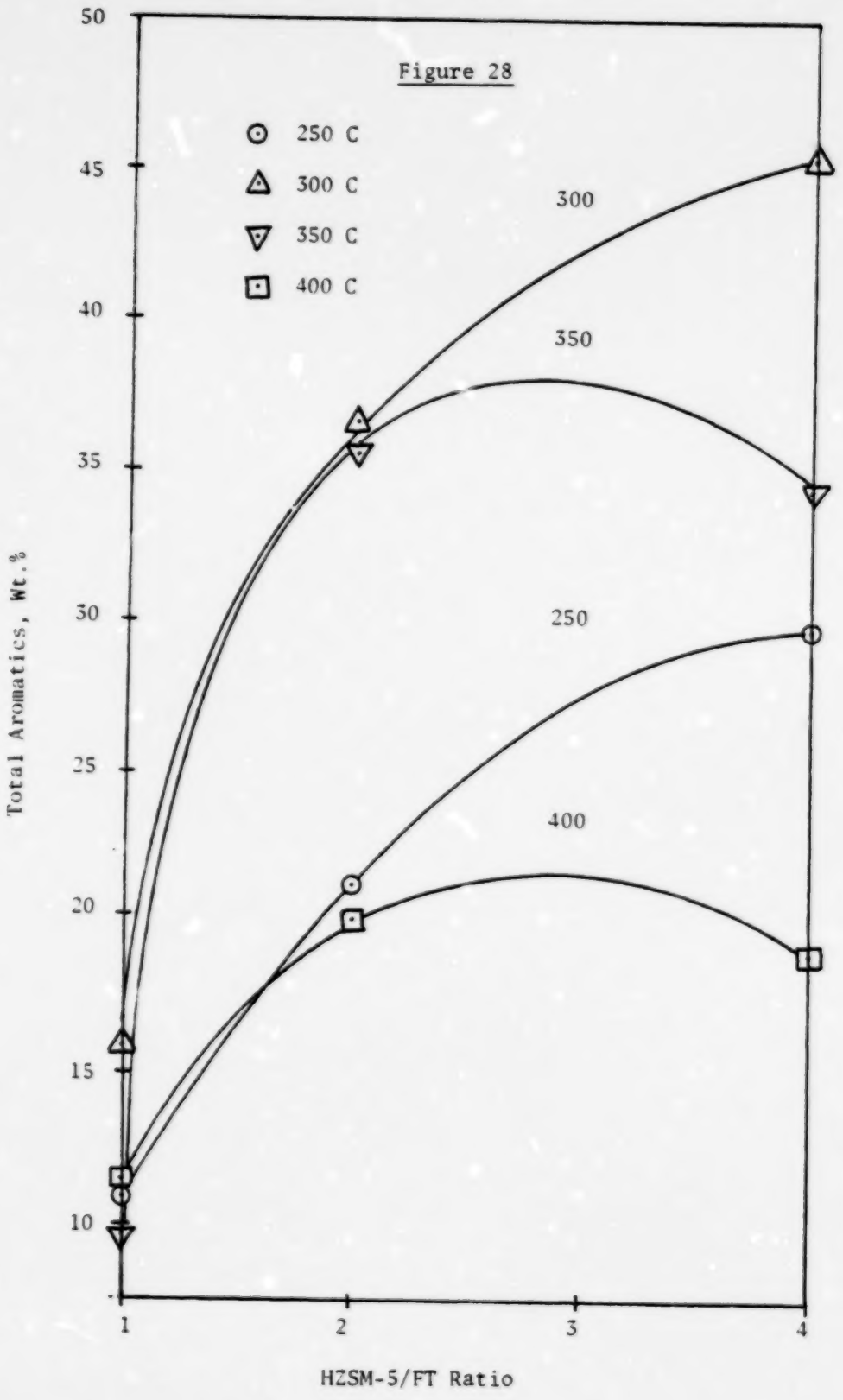
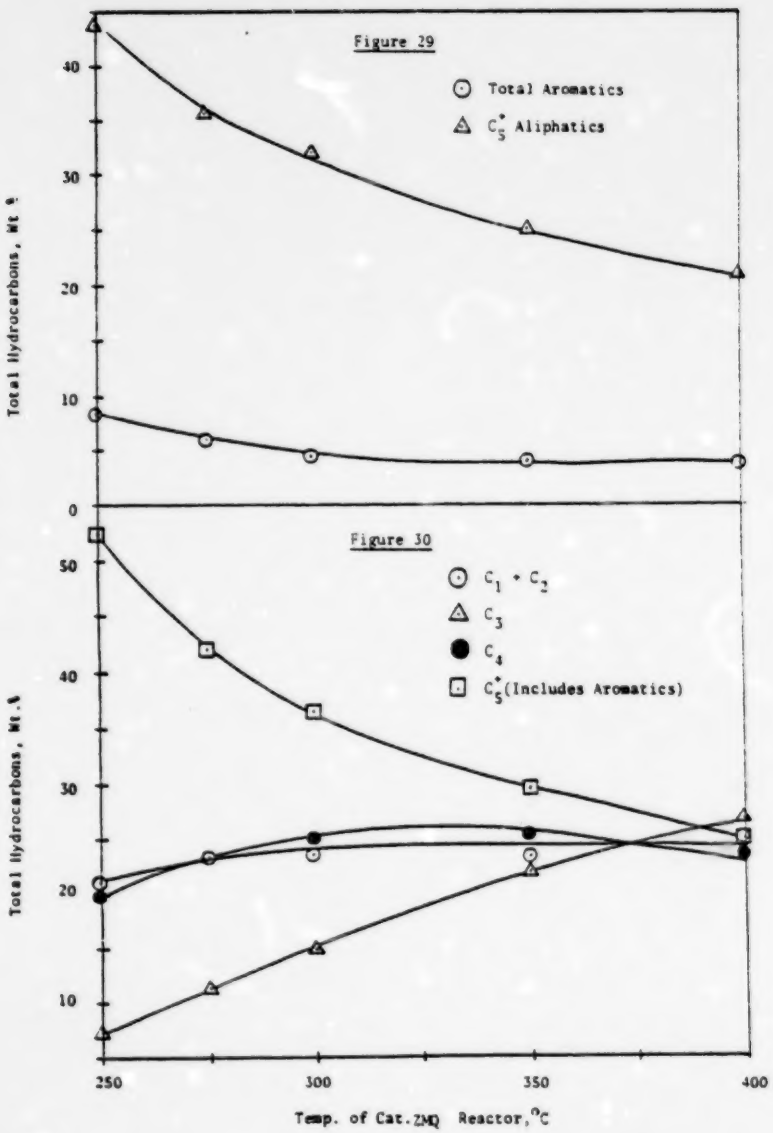
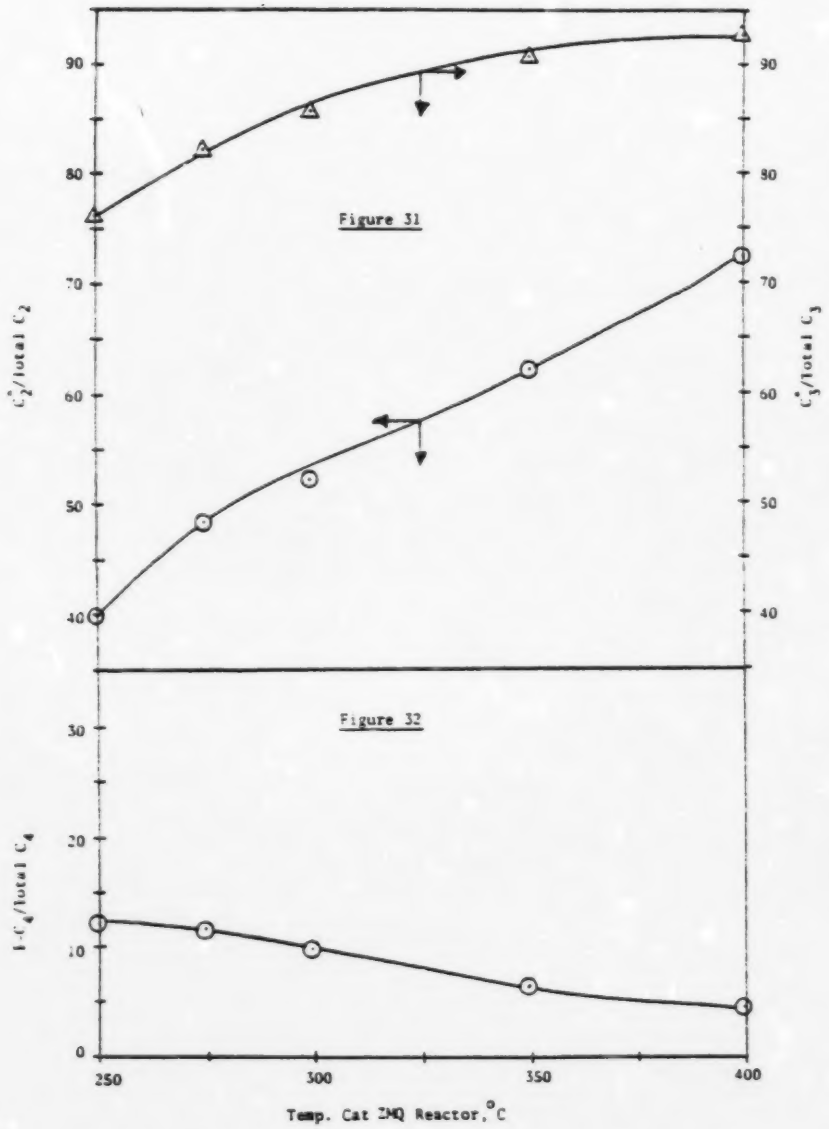


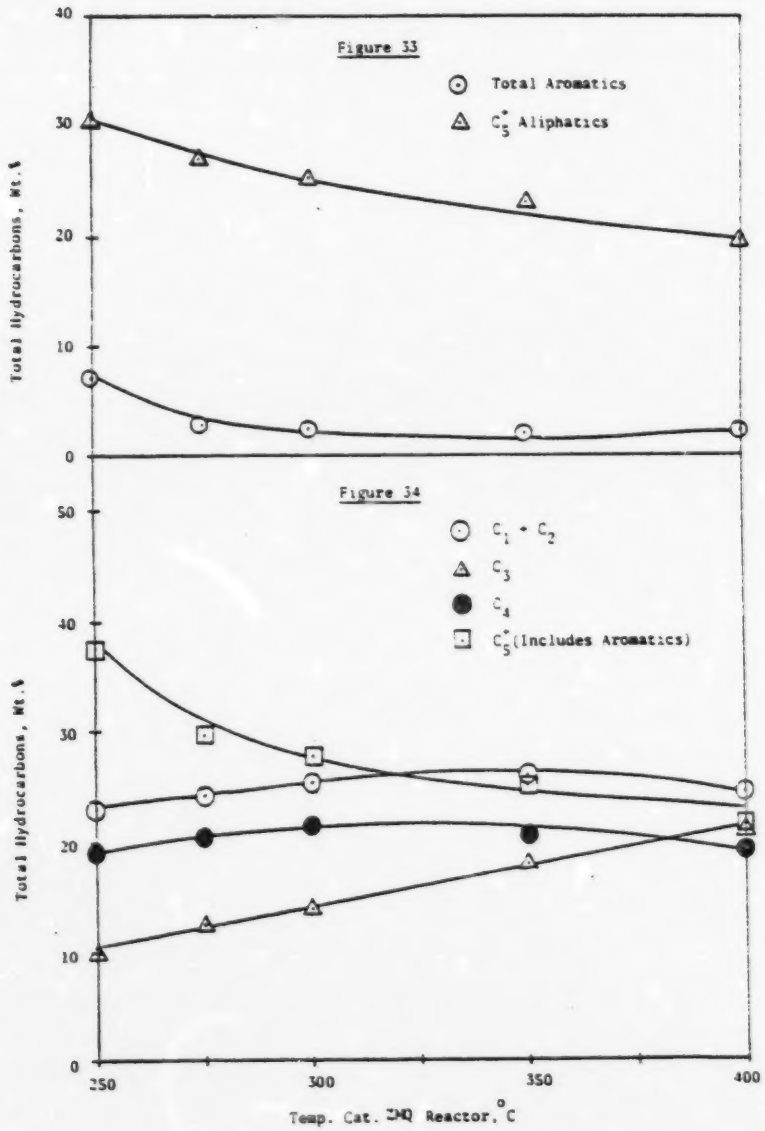
Figure 28. Variation of Total Aromatics with HZSM-5/FT Ratio.



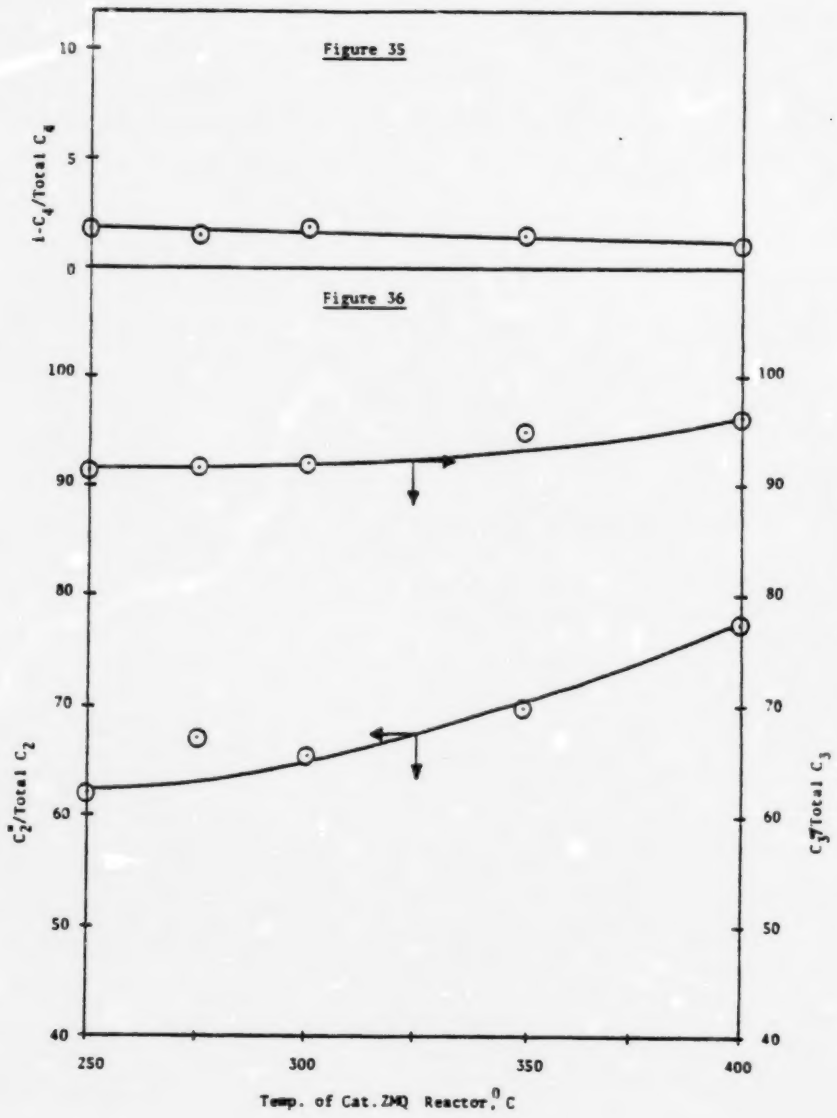
Figures 29 & 30. Variation of product Distribution with Temperature of Catalyst ZMQ Reactor, Catalyst ZMQ/FT = 4



Figures 31 & 32. Variation of C_2-C_4 Distribution with Temperature Of Catalyst ZMQ Reactor , Catalyst ZMQ/FT = 4



Figures 33 & 34. Variation of Product Distribution with Temperature of Catalyst ZMQ Reactor, Catalyst ZMQ/FT = 1



Figures 35 & 36. Variation of C_2-C_4 Distribution with Temperature of Catalyst ZMQ Reactor, Catalyst ZMQ/FT = 1

Summary of experimental runs for Task F: (1/2" Packed Bed Reactor)

Ranges of Operating Conditions						Analysis of a typical run											
						Operating Conditions											
Run No.	Temp °C	CO/H_2	FT Cat g	HZSM-5 (or) ZMQ g	Exit flow rate ml./min	Typical Run No.	CO Conv. %	Temp °C	CO/H_2	FT cat wt. g	HZSM-5 (or) ZMQ g	Exit flow rate ml/min	C_1	C_2	C_3	C_4	C_5^+ (incl. aromatics)	Total Aromatics
422-455 (with HZSM-5)	225-300	1,2,3	0.9999	4.0002	5.2-95.2	445	3.9	250	1.0	0.9999	4.0002	5.1	18.7	2.6	9.0	22.6	47.1	21.6
456-498 (with HZSM-5)	250	1.0	4.000	11.8245	21.4	461	13.0	250	1.0	4.000	11.8245	21.4	15.1	1.0	13.2	22.3	48.4	30.5
499-533 (FT alone)	250	1.0	4.000	0.0	20.5	511	25.3	250	1.0	4.000	0.0	20.5	22.5	4.4	9.0	8.2	50.9	0.0
534-558 (with ZMQ)	250, 300	1.0	4.0001	12.000*	21.0	547	30.3	250	1.0	4.0001	12.000*	21.0	20.9	3.4	6.5	19.9	49.3	11.8

* Wt of ZMQ

Summary of experimental runs for Task G: (Dual-Bed Microreactor)

Ranges of Operating Conditions							Analysis of a typical run										
	Temp °C								Temp °C								
Run No.	FT	HZM-5 or ZMQ	CO/H_2	FT Cat q	HZSM-5 or ZMQ q	Exit flow rate, mL/min	Typical run No.	CO Conv., %	FT	HZSM-5 (or) ZMQ	CO/H_2	Exit flow rate, mL/min	C_1	C_2	C_3	C_4	C_5 (incl. aromatics)	Total Aromatics
577-629 (with HZSM-5)	250	250-400	1.0	0.1004	0.1005	9.9-11.6	585	7.6	250	250	1.0	9.9	16.4	3.0	11.2	25.0	44.4	10.9
630-680 (with HZSM-5)	250	250-400	1,2,1	0.1000	0.3999	7.4-9.4	648	9.8	250	250	1.0	8.5	16.0	2.1	9.6	20.6	51.6	12.2
681-696 (with HZSM-5)	250	250-400	1.0	0.1001	0.2004	8.6-9.8	687	7.0	250	250	1.0	9.1	18.1	2.4	9.5	20.6	49.3	11.2
697-732 (with ZMQ)	250	250-400	1.0	0.1000	0.4000*	4.1-4.9	706	11.6	250	250**	1.0	4.9	17.8	2.7	7.4	19.8	52.3	8.6
735-761 (with ZMQ)	250	250-400	1.0	0.1003	0.1004*	5.3-6.7	742	8.2	250	250**	1.0	5.3	18.9	4.1	9.9	19.2	47.9	7.1

* Wt of ZMQ

** Temp of ZMQ